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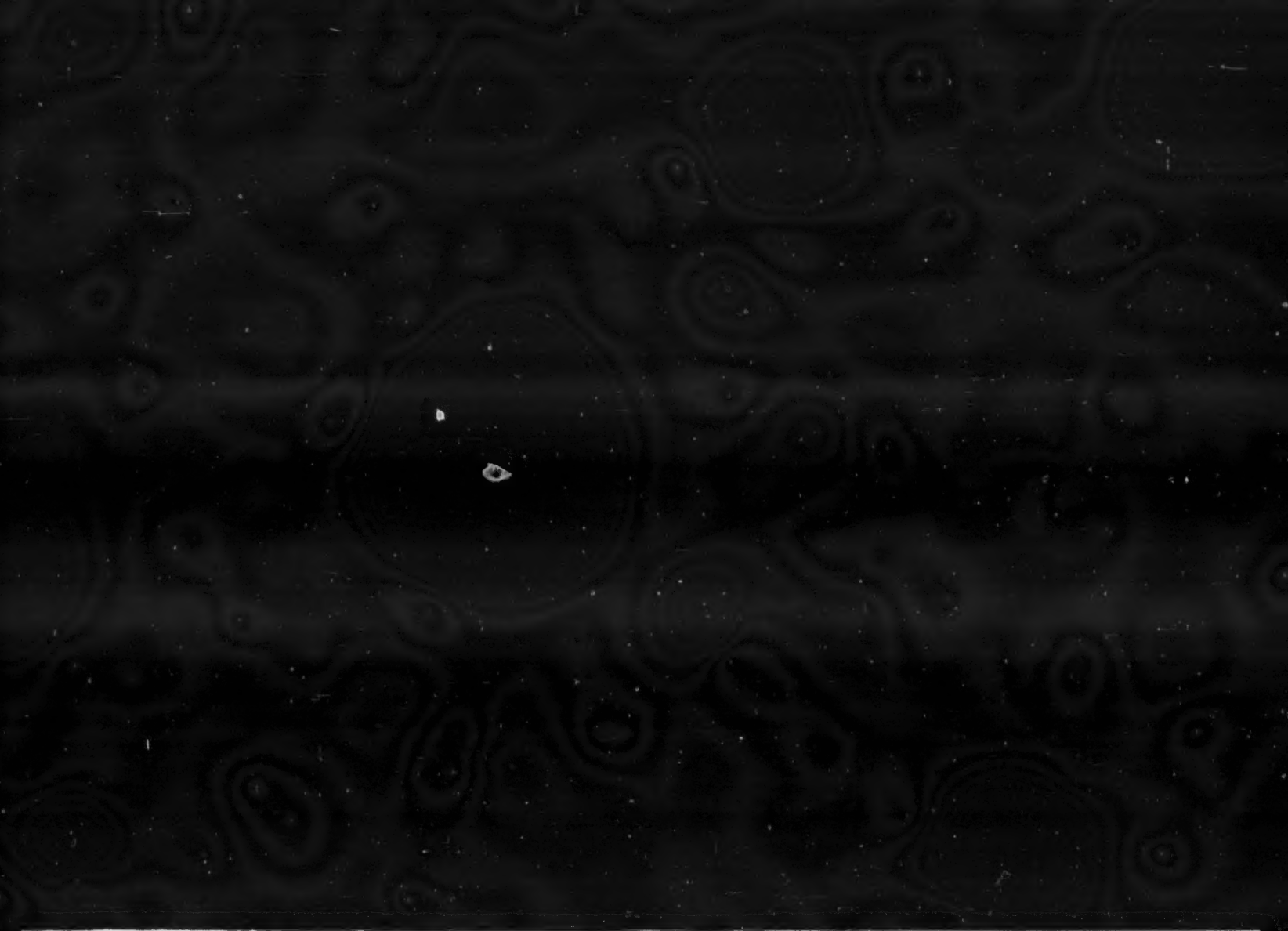

THE AGEING OF AQUEOUS SUSPENSIONS OF MAGNESIUM HYDROXIDE

by

G. J. R. KRIGE and R. ARNOLD

OPSOMMING

Die konsentrasie van 'n vars-bereide waterige oplossing van magnesiumhidroksied wat 'n oormaat van die vaste stof bevat, verminder nog vir maande na die bereiding daarvan. Hierdie verskynsel is ondersoek deur die verandering in geleidingsvermoë te volg wat plaasvind in sulke suspensies, wat berei was deur óf magnesiumoksied óf magnesiumamalgaam op water te laat inwerk. Suspensies berei volgens hierdie metodes is kolloïdaal. Dit is bewys dat die proses van veroudering autokatalities is. Die lae temperatuurkoëffisiënt van die verouderings-proses elimineer die moontlikheid dat enige chemiese reaksie die spoed-bepalende faktor is. Daar is 'n duidelike aanduiding dat die temperatuurkoëffisiënt van die oplosbaarheid van varsbereide hidroksied negatief is. Geen bewyse is gevind vir die bestaan van 'n metastabiele vorm van magnesiumhidroksied met 'n definitiewe oplosbaarheid nie. Dit is gevind dat die oplosbaarheid van verouderde magnesiumhidroksied $1{\cdot}52 \times 10^{-4}$ moles per liter by 20°C. bedra. Die noodsaaklikheid van verdere ondersoek i.v.m. hierdie probleem word beklemtoon.

SUMMARY

The concentration of a freshly prepared aqueous solution of magnesium hydroxide, containing excess solid, decreases for several months after its preparation. This phenomenon has been investigated by following the conductivity changes which take place in such suspensions, which were prepared by adding either magnesium oxide or magnesium amalgam to water. Suspensions prepared by these methods are colloidal. It is shown that the ageing process is autocatalytic. The low temperature coefficient of the ageing process excludes any chemical reaction as being the rate determining process. An indication is obtained that the temperature coefficient of solubility of the freshly prepared hydroxide is negative. No evidence is obtained for the existence of a metastable form of magnesium hydroxide with a definite solubility. The solubility of aged magnesium hydroxide is found to be $1{\cdot}52 \times 10^{-4}$ moles per litre at 20°C. The need for further investigation is emphasized.

INTRODUCTION

The fact that the concentration of a saturated solution of magnesium hydroxide decreases for some time after the preparation of the solution, was apparently first noticed in 1866 by Pribram[1]. Since then, several investigators[2] reported the same phenomenon, but no attempts at explanation were forthcoming until Le Blanc and Richter[3] in 1923 suggested that the decrease with time in the electrical conductivity of the system obtained by adding magnesium oxide to water was due to the gradual hydration of the oxide. Remy and Kuhlmann[4], on the other hand, attributed this behaviour to the absorption of carbon dioxide by the suspension.

Gjaldbaek[5] investigated the pH changes which took place in magnesium chloride solutions to which had been added either sodium hydroxide, magnesium oxide, or magnesium turnings. From the results obtained in these experiments he concluded that there exist both "labile" and stable forms of the hydroxide, each having a well-defined solubility. He also calculated the solubility of these two forms, and gives in his paper a review of all previous determinations of the solubility of magnesium hydroxide. W. Busch[6] reported a series of solubility determinations carried out on magnesium hydroxide prepared by adding the oxide to water. Comparing his results with those of Gjaldbaek and other investigators, Busch came to the conclusion that the final constant solubility is not a fixed quantity, but depends on the source from which the magnesium hydroxide was obtained.

X-ray analysis has failed to show any difference between the crystal structures of magnesium hydroxide samples of different ages[7], but has revealed an increase in particle size with time[8].

Thus there still remains some doubt both as to the solubility of magnesium hydroxides and as to the nature of the ageing process which it undergoes. Many investigators have worked with the hydroxide in the presence of salts, which are known to affect considerably both the solubility[9] and the rate of change of solubility[5]. Gjaldbaek did carry out one experiment on a pure aqueous suspension of magnesium oxide, but was in this case unable to obtain a constant pH value after twenty-three days. A further investigation has therefore been carried out on the ageing of this hydroxide by following the conductivity changes which occur in suspensions prepared by adding either magnesium amalgam or magnesium oxide to water.

Materials Used

(*a*) *Conductivity water.* Ordinary distilled water was redistilled, using a tin condenser fitted with a spray-trap. The distillate was transferred to the conductivity cell in which it was to be used, where it was further purified by passage of nitrogen or oxygen which had been carefully freed from acid or alkaline impurities. The water thus produced had a conductivity at 20°C. of $0{\cdot}4 - 1{\cdot}0 \times 10^{-6}$ mho.

(*b*) *Magnesium ribbon.* This was used as starting material for preparing the amalgams and some of the oxide samples. It was found to contain small amounts of iron and manganese, which together amounted to about 0·1 per cent. Traces of carbon were also detected. No other impurities were found by examination of the flame spectrum.

(*c*) *Magnesium amalgam.* The amalgams used varied in concentration, but usually contained 0·1 – 0·3 per cent magnesium. Such dilute amalgams may be prepared by simply shaking magnesium metal and mercury together; if the surface of the magnesium is clean, amalgamation is complete within about five minutes, and takes place with the liberation of an appreciable amount of heat. The surface of the magnesium ribbon was cleaned with a steel knife, and redistilled mercury was used.

In order to minimize decomposition of the amalgams by air, the samples were prepared in small ignition tubes closed with waxed corks, and were not mixed until about ten minutes before use. It was found that less of the amalgam stuck to the sides of the tube if the latter was internally coated with paraffin wax before use.

(*d*) *Magnesium oxide from magnesium nitrate.* Cleaned magnesium ribbon was dissolved in dilute nitric acid, the solution evaporated to dryness, and the residue decomposed by strong heating. The product was broken up with a steel knife, and then reignited in a full Méker flame, in order to decompose any carbonate formed during this operation. After ignition the product was kept in a desiccator over solid sodium hydroxide.

(*e*) *Magnesium oxide from the precipitated hydroxide.* In preparing magnesium oxide by precipitation, magnesium chloride and ammonia were chosen as reactants, since the resulting impurities should then be volatile. An aqueous solution of magnesium chloride was treated while boiling with a considerable excess of dilute ammonium hydroxide. The precipitate was washed with hot water until free from chloride, oven dried, and transferred to a platinum crucible. The product thus obtained was ignited over a Méker burner, ground in a small agate mortar, returned to the platinum crucible, and reignited to constant weight. The oxide was stored over sodium hydroxide.

EXPERIMENTAL

According to Gjaldbaek[5] magnesium hydroxide suspensions slowly attack glass, with formation of silicate. The glass parts of the conductivity cells and electrodes were therefore coated with paraffin wax. In a few experiments, where the conductivity changes were to be followed only for a few days, this precaution was omitted.

Conductivities were measured by a simple Wheatstone bridge circuit. Current of one thousand cycles frequency was obtained from a tuning-fork oscillator, and a telephone receiver was used as detector.

The procedure adopted in determining the effect of time on the conductivity of the suspensions was generally as follows. Pure nitrogen or oxygen was bubbled through conductivity water in the cell, the gas finally escaping through a soda-lime tube. When the conductivity of the water had fallen to a steady value below 1×10^{-6} mho, the sample of oxide or amalgam was quickly introduced through a glass tube passing through the stopper of the cell, which was then quickly resealed with a waxed cork.

As a final precaution against contamination by carbonate, the oxide samples were each reignited immediately before use for at least five minutes, for which purpose they were placed on a small platinum foil. Only about thirty seconds' time was allowed for cooling before adding the samples to the water in the cell.

Conductivity readings were carried out at 20·0°C., except where otherwise stated. In the ageing experiments, however, this temperature was maintained only during the day; at night the thermostat was switched off, and in the mornings the temperature had generally fallen one to three degrees below 20°C. Passage of nitrogen or oxygen was continued throughout the experiments.

RESULTS

(*a*) Action of water on magnesium amalgam

On the addition of magnesium amalgam to water a vigorous reaction takes place, and a dark grey opaque suspension is rapidly formed. On standing, the colour becomes lighter, and finely-divided mercury settles out. The suspension still contains colloidal matter, however, for it exhibits a white opalescence, and a faint brown tint by transmitted light; a marked Brownian movement may also be detected. Cataphoretic experiments showed the sol to be electropositive, like most sols of metallic oxides. If left exposed to the atmosphere the colloidal matter coagulates within about two hours, whereas the sol is stable in absence of carbon dioxide for at least ten weeks.

(*b*) Effect of time on the conductivity of magnesium hydroxide suspensions

Altogether six experiments were carried out on the ageing at 20°C. of suspensions prepared from magnesium amalgam and water. The conductivity-time curves thus obtained were all very similar, and only the early stages of two of them are reproduced here, being curves 5 and 6 of Figure 1. Some results of these experiments are given in Table 1.

Although readings were taken two to six minutes after addition of the amalgam, the first readings nevertheless correspond in all cases to the highest conductivities recorded. Thus the reaction between the amalgam and the water is rapid. It will be noticed that a steep fall in conductivity occurs in the initial stages, followed by a gradual approach to equilibrium. In all the experiments a slight but unmistakable inflection was observed in the time-conductivity curves, at approximately the twenty-four ordinate. At this stage there is evidently a sudden increase in the rate of fall of conductivity.

Six similar experiments were carried out with magnesium oxide. While all the time-conductivity curves obtained show the same essential features, the rates of the

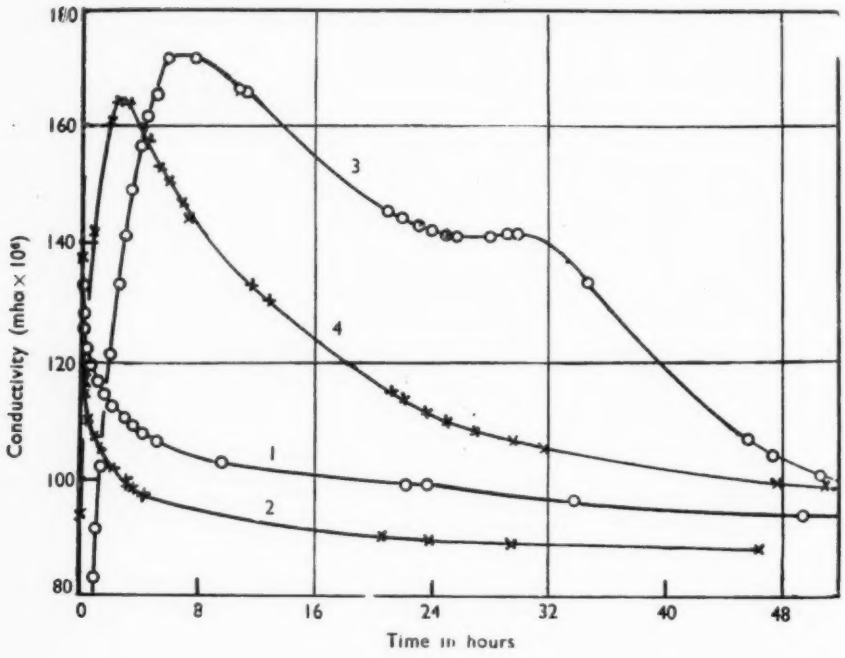

FIG. 1
Time-conductivity curves for magnesium hydroxide suspensions. (The numbers attached to the curves correspond to the experiment numbers in Tables I and II.)

TABLE I

Ageing experiments at 20°C. using magnesium amalgam.

Experiment	*Amount of amalgam added*	*Volume of water (ml.)*	*Highest conductivity observed (mho × 10⁶)*	*Final conductivity (mho × 10⁶)*	*Final time (hours)*
1	Not measured	800	130·7	88·3	120
2	Not measured	800	133·1	86·3	240
3	7·6 g. of 0·124 per cent ...	40	138·6	87·2	150
4	15·6 g. of 0·124 per cent ...	40	144·6	88·6	150
5	20·0 g. of 0·25 per cent ...	100	142·0	85·4	622
6	4·0 g. of 0·25 per cent ...	100	140·5	82·1	530

different processes occurring evidently depend to a considerable extent on the precise conditions under which the oxide is prepared. A close control of these conditions would have to be instituted before an interpretation of their effect could be obtained. Curves 7, 10 and 12 of Fig. 1 are examples of the earlier parts of the conductivity-time

curves obtained in these experiments, while Table II records some of the more important results of all six experiments.

TABLE II

Ageing experiments at 20°C. using magnesium oxide.

Experiment	*Source of MgO*	*Weight of MgO (g.)*	*Volume of water (ml.)*	*Maximum conductivity (mho × 10^6)*	*Time at which maximum attained (hours)*	*Final conductivity (mho × 10^6)*	*Final time (hours)*
7	Nitrate	0·08	100	172	25	93·8	680
8	Nitrate	0·15	100	161	24	—	—
9	Nitrate	0·06	100	153	42	—	—
10	Hydroxide	0·05	100	172	6	87	120
11*	Hydroxide	0·06	100	163	21	—	—
12*	Hydroxide	0·25	100	181	7	—	—

* In experiments 11 and 12, samples of magnesium oxide from the same stock were used; all other experiments were carried out with different preparations.

(*c*) The effect of the amount of solid phase and of temperature on the rate of change of conductivity

Two conductivity cells were constructed in such a way that the stream of neutral gas could be passed through them in series. The ageing of two suspensions could thus be followed concurrently, under comparable conditions of temperature and rate of stirring. With this apparatus experiments were carried out at 10°C., 20°C. and 30°C. In each case 20 g. of 0·25 per cent magnesium amalgam was added to one cell, and 4 g. of 0·25 per cent amalgam to the other, the volume of water being always 100 ml. The ageing at 20°C. was followed for twenty-five days, the changes occurring in the early stages being shown by curves 5 and 6 of Fig. 1. The experiments at 10°C. and at 30°C. were only continued for twenty-six hours, temperature control being maintained throughout. For purposes of comparison, however, at the conclusion of these experiments the temperature was adjusted to 20°C. and a few more measurements taken; *see* Table III.

The conductivity changes which occurred during the first twenty-six hours of these experiments are shown by Fig. 2. It will be noticed that for each temperature the smooth curve obtained for the more concentrated suspension lies above the dotted curve which refers to the more dilute suspension. Furthermore, examination of each pair of curves corresponding to a particular temperature reveals only a slight tendency towards convergence. This leads to the following conclusions regarding the effect of the amount of solid phase. On adding the amalgam to the water, two processes occur: a rapid decomposition of the amalgam to form hydroxide in a highly soluble condition, followed by a slower process whereby the latter is converted to a less soluble condition. The rate of formation of hydroxide is increased by taking a larger amount of amalgam, whereas the process which brings about the decrease in conductivity is evidently not appreciably affected by the amount of solid phase. Thus the more concentrated suspension attains a higher initial concentration, and maintains this higher value during the ageing process.

In the experiments in which magnesium oxide was used, only two are at all comparable in that they were carried out with oxide samples from the same stock (experiments 11 and 12, Table II). Here, too, the more concentrated suspension attained a higher

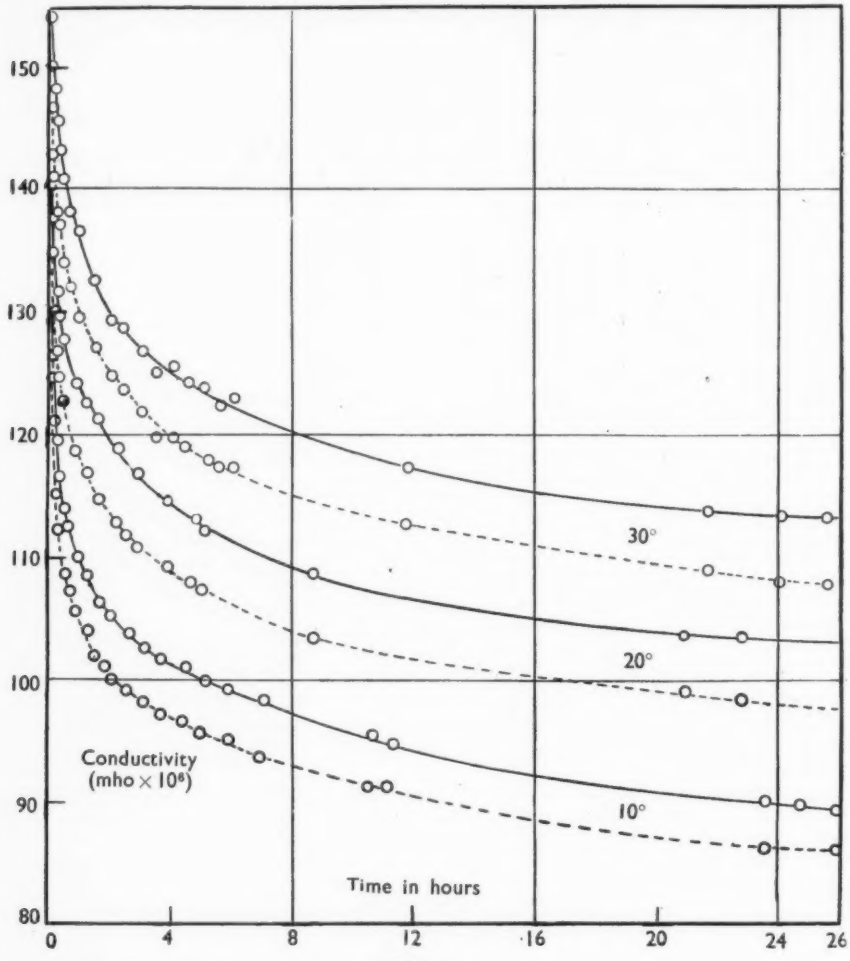

FIG. 2

Effect of temperature and amount of solid phase on the ageing of magnesium hydroxide suspensions. Full lines refer to concentrated suspensions. Dotted curves refer to dilute suspensions.

initial conductivity, but ageing was more rapid in the case of the concentrated suspension than with the dilute sample. The slow hydration of the oxide is probably a complicating factor here.

The effect of temperature may now be considered. The results shown in Table III give a qualitative indication of the fact that increase in temperature accelerates the ageing process.

TABLE III

Effect of temperature on the extent of ageing of magnesium hydroxide suspensions.

Weight of 0·25 per cent amalgam (g.) per 100 ml. H_2O	*Treatment*	*Conductivity at 20°C. (mho × 10^6)*
20	26 hours at 10°, then 5 hours at 20°	108·4
20	31 hours at 20°	102·3
20	26 hours at 30°, then 5 hours at 20°	96·9
4	26 hours at 10°, then 5 hours at 20°	104·1
4	31 hours at 20°	96·6
4	26 hours at 30°, then 5 hours at 20°	92·1

Thus the higher the temperature of initial treatment, the lower the conductivity subsequently obtained at 20°C., and hence the greater the extent of ageing.

In order to obtain quantitative data for the temperature effect, tangents were drawn to the curves in Fig. 2 at points corresponding to 0·5, 1·0 and 2·0 hours after addition of the amalgam. For any two curves corresponding to suspensions of the same concentration and to temperatures 10° apart, the ratio of the tangents at the same time-ordinate gives the temperature coefficient, $k_{(t+10)°}/k_{t°}$. The results obtained are shown in Table IV.

The results, although erratic (due in part to the difficulty of drawing tangents accurately), indicate that the temperature coefficient of the ageing process lies between 1·0 and 1·2, and is thus of the magnitude typical of physical processes such as diffusion. Since for most chemical reactions the temperature coefficient of reaction velocity lies above 2, it is improbable that hydration of magnesium oxide is the change which is responsible for the fall in conductivity, as was suggested by Le Blanc and Richter[3].

Qualitative information about the effect of temperature on the solubility of magnesium hydroxide may also be obtained from these experiments. Although no maximum conductivity was actually observed (due to the rapidity with which the ageing process began), we may take the conductivity three minutes after addition of amalgam as a rough measure of the maximum conductivities attained. From these conductivities (obtained where necessary by extrapolation) the corresponding concentrations of magnesium hydroxide have been calculated. For this purpose complete dissociation has been assumed, and the values for the equivalent conductance of magnesium hydroxide at infinite dilution obtained from the literature, the values used being 180·1, 228·5 and 276·8 mho at 10°, 20° and 30° respectively. The results obtained are shown in Table V.

The interesting result is that the concentrations so found decrease with rising temperature. Since rates of reaction and of solution are always increased by rise in temperature, the most probable explanation of this result is that the solubility of freshly-formed magnesium hydroxide decreases with rising temperature and should possess a negative temperature coefficient. It may be noted that Travers and Nouvel[10] actually found such a negative temperature coefficient for the solubility of magnesium hydroxide, but did not state the age of their product, while Gjaldbaek[5] found the reserve for aged magnesium hydroxide, namely, a rise in solubility with temperature.

A further investigation of the effect of temperature on the solubility of magnesium hydroxide is therefore desirable.

TABLE IV

Temperature coefficients of the rate of ageing.

Weight of 0·25 per cent amalgam (g.)	*Temperature (°C.)*	*Time (hours)*	*Tangent*	*Temperature coefficient*
20	10	0·5	1·50	0·91
20	20	0·5	1·37	
20	30	0·5	1·67	1·22
20	10	1·0	0·70	0·70
20	20	1·0	0·50	
20	30	1·0	0·86	1·72
20	10	2·0	0·31	1·16
20	20	2·0	0·36	
20	30	2·0	0·43	1 19
4	10	0·5	1·35	1·01
4	20	0·5	1·37	
4	30	0·5	1·70	1·24
4	10	1·0	0·62	1·07
4	20	1·0	0·66	
4	30	1·0	0·74	1·12
4	10	2·0	0·31	1·03
4	20	2·0	0·32	
4	30	2·0	0·44	1·38

TABLE V

Effect of temperature and ratio amalgam to water on the maximum concentration reached in magnesium hydroxide suspensions.

Weight of 0·25 per cent amalgam (g.)	*Temperature (°C.)*	*Conductivity after 3 minutes (mho × 10⁶)*	*Concentration (mole/litre × 10⁴)*
20	10	134	3·72
4	10	126	3·51
20	20	143	3·13
4	20	140	3·07
20	30	155	2·80
4	30	151	2·73

(*d*) The autocatalytic effect

It has been pointed out that inflections were observed in the time-conductivity curves, these being slight where magnesium amalgam was used but pronounced in the curves referring to suspensions prepared from the oxide. These inflexions could merely mark the completion of the hydroxide-forming process, or they could be due to an autocatalytic effect. A combination of these two effects might also be responsible for the inflexions.

Further information on this point was therefore sought by determining the rate of ageing of fresh magnesium hydroxide in the presence of an old sample of the hydroxide, as in the following experiments:—

(i) At the conclusion of one of the experiments using suspensions prepared from amalgam (Table I, experiment 2), thirteen days after the first addition, a second sample of amalgam was added to the same suspension. Curves 1 and 2 of Fig. 3 represent the conductivity readings recorded after the first and second additions of amalgam, respectively.

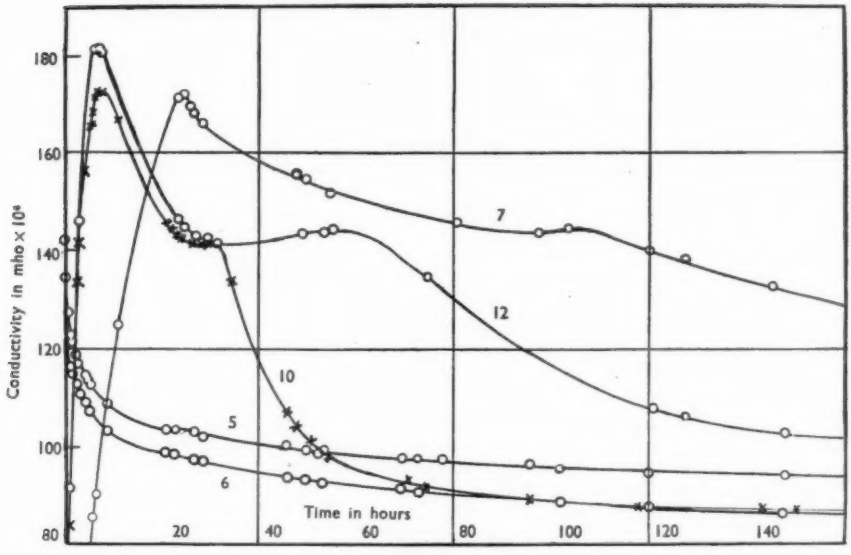

FIG. 3
Addition of oxide and amalgam to aged suspensions.

It will be seen that the conductivity rose rapidly from that of the aged suspension to a value ($137 \cdot 5 \times 10^{-6}$ mho) typical of the highest values recorded in the other experiments with amalgam. The fall of conductivity which then ensued, however, was much more rapid than that observed when amalgam was added to pure water, and no inflexion could be detected.

(ii) Similarly, at the conclusion of an experiment with magnesium oxide obtained by precipitation (Table II, experiment 10), thirteen days after the first addition

of oxide, a further sample of the same oxide was added. Curves 3 and 4 of Fig. 3 refer to the results of the first and second additions respectively. These results are similar to those obtained with the amalgam in experiment (i) above.

The volume of water used was 100 ml., and the weights of oxide were 0·05 g. in the first ageing and 0·04 g. in the second.

(iii) The same procedure was carried out with another sample of precipitated oxide, the second sample being added seven days after the first. In this case, however, the second ageing process gave a time-conductivity curve roughly coincident with that referring to the first ageing, the results of which have been represented by curve 12 of Fig. 1. The weights of oxide used per 100 ml. of water in the first and second additions were 0·17 and 0·14 g. respectively.

The nature of the inflexions observed in the time-conductivity curves may now be discussed in the light of these experiments.

Shortly after addition of magnesium oxide to water, two processes will occur:— (1) the hydration of the oxide with formation of hydroxide in a highly soluble condition; and (2) the reversion of this hydroxide to a less soluble condition. The first process will tend to raise the conductivity and the second to lower it. Campbell[11] found that magnesia prepared by burning magnesite at 600–800°C. required three days for complete hydration*; with increasing temperature of ignition the time for hydration increases considerably. Thus the sudden increase in the rate of fall of conductivity observed thirty to one hundred hours after adding the oxide to water could be explained as due to completion of the hydration process, *i.e.*, of the process tending to raise the conductivity. That the formation of highly soluble hydroxide does continue for some time is certainly confirmed by the fact that the conductivity generally rose slightly just before the inflexions, in the experiments with oxide. (It would be of some interest to determine the temperature coefficient of the process at this stage.)

This mechanism alone is, however, inadequate to explain the results of experiments (i) and (ii) above, which indicate that the presence of aged particles accelerates that process which leads to a decrease of conductivity. The inflexions must therefore be due partly to the catalytic effect of the aged particles.

In the case of the suspensions prepared from amalgam, inflexions could again be due to cessation of the decomposition of the amalgam together with the autocatalytic effect. The inflections occurred about twenty-four hours after addition of amalgam, and since the reaction between the amalgam and water appears to last only a few minutes, it may be that here the autocatalytic effect alone is operative.

We now have to consider the fact that no catalytic effect was apparent in the experiment (iii) of this section. The following are possible explanations:—

(1) The suspension was not sufficiently aged before adding the second sample, only seven days having elapsed after the first addition as opposed to thirteen days in the other two experiments. This does not seem a likely explanation since the inflexion had long been passed at this stage.

(2) The two samples of oxide used in (ii) and (iii) above were different in condition, the sample used in the last experiment, where no catalysis was shown, being less active than the other, in that it gave rise to slower rates of solution and of ageing. It may be mentioned that in the preparation of this less active oxide the precipitated hydroxide was left over solid sodium hydroxide for seventeen months before ignition to the

* The time of hydration must depend on the particle size of the sample, as well as on the temperature to which it has been heated.

oxide. The precise nature and effect of the differences between the two oxide samples is not understood.

(3) Owing partly to the larger amount of oxide used and partly to a different rate of hydration, the formation of highly soluble particles continued for a longer time and at a greater rate in the last experiment. Compare the extents of the more or less horizontal portions before the inflexions in curves 10 and 12 of Fig. 1, which represent the first portions of experiments (ii) and (iii) of this section respectively. Thus the hydration effect may have swamped the autocatalytic effect in the last experiment. This seems the most probable explanation.

It may be mentioned that a sample of precipitated oxide was also added to a $4{\cdot}2\times10^{-4}$ molar solution of magnesium chloride, *i.e.*, a solution containing magnesium ions at about the same concentration as in the aged suspension. The sample of oxide was from the same stock as that used in experiment (iii) above, and about the same proportions were used (0·18 g./100 ml.). The time-conductivity curve obtained was of essentially the same form as that obtained with pure water, except that the inflexion was slightly less marked. No positive inference can therefore be drawn.

(*e*) The effect of the presence of gelatin on the conductivity changes of magnesium hydroxide suspensions

In an attempt to stabilize the abnormally soluble magnesium hydroxide, 40 g. of 0·125 per cent magnesium amalgam was added to 200 ml. of 0·1 per cent gelatin solution, the conductivity of which at 20°C. was $3{\cdot}1\times10^{-6}$ mho. The only noticeable effect of the gelatin was that the conductivity rose more slowly than usual, so that for the first time with amalgam a maximum was actually observed. Thus after three minutes the conductivity was still rising, and after six minutes the maximum value, $135{\cdot}3\times10^{-6}$ mho, was recorded.

(*f*) Final conductivity of aged magnesium hydroxide suspensions

The final conductivities observed in the experiments thus far reported varied from 82 to 94×10^{-6} mho at 20°C. Better agreement would be expected if these values corresponded to the final equilibrium value for the stable hydroxide. It is probable therefore that these measurements were taken when conductivity changes were still taking place, but too slowly to be detected*. Further experiments were therefore carried out to determine the conductivity of stable suspensions.

(i) A sample of magnesium amalgam was added to carbon dioxide-free water in a small pyrex bottle, which was then sealed. This sample retained its colloidal appearance for two and a half months, after which settling occurred. At this stage the bottle was opened and the contents quickly poured into a small dry conductivity cell through which nitrogen was passing. The conductivity observed was $70{\cdot}9\times10^{-6}$ mho at 20°C.

(ii) A similar experiment was carried out with magnesium oxide obtained by igniting the nitrate. Here, however, a waxed vessel was used, and the ageing continued for only two months. At the end of this period the conductivity at 20°C. was $75{\cdot}7\times10^{-6}$ mho, and Brownian movement could still be detected.

(iii) To obviate the necessity of transferring the suspension and thus incurring the danger of carbon dioxide absorption, use was made of a conductivity pipette. This was passed through a waxed cork, which was also provided

* In a few cases a slight increase in conductivity began after about a month, due no doubt to a leak in the apparatus or to failure of the gas-purifying train, thus allowing of the formation of carbonate.

with inlet and outlet tubes for gas, both being fitted with glass taps. Suspensions were prepared in 200 ml. pyrex flasks, which fitted on to the cork holding the conductivity pipette. Thus, conductivity water was first placed in the flask, and nitrogen passed until a minimum conductivity was reached. Thereupon the flask was withdrawn, a sample of magnesium oxide added, and the flask immediately corked and sealed with wax. As a further precaution the flasks were stored in an air-tight container in which solid sodium hydroxide was exposed.

The samples thus prepared were kept for nearly five months, after which they were brought to 20·0°C., opened and refitted to the conductivity apparatus, which had previously been filled with pure oxygen. A sample was drawn into the pipette (to the top of which a soda-lime tube was sealed) and the conductivity measured. In this way the suspensions were exposed to the atmosphere for only about twenty seconds.

Six suspensions were prepared in this way, all from the same stock of precipitated oxide. Three were in unwaxed pyrex flasks, and three in waxed flasks. At the end of five months the samples in the unwaxed flasks showed no Tyndall effect, and gave very low and discordant conductivities, namely, 31·6, 38·6 and $45·2\times10^{-6}$ mho. Those in the axed flasks, on the other hand, showed very distinct Tyndall effects, were slightly opalescent, and gave fairly consistent results. The conductivities and other details are given in Table VI.

TABLE VI

Conductivity of magnesium hydroxide suspensions after long ageing.

Weight of oxide (g.)	*Volume of water (ml.)*	*Conductivity of water used (mho × 10⁶)*	*Time of ageing (days)*	*Final conductivity at 20°C. (mho × 10⁶)*
0·09	175	0·6	147	71·9
0·13	175	0·6	147	69·5
0·14	175	0·8	146	69·9

One sample of water was treated in the same way, without addition of oxide, to serve as a blank. The conductivity, $0·4\times10^{-6}$ mho, was unchanged after 111 days' storage.

It will be seen that the final conductivities observed (experiment (iii)) agree moderately well amongst themselves and with that obtained previously (experiment (i)) with the amalgam, *i.e.*, $70·9\times10^{-6}$ mho. The higher result, $75·7\times10^{-6}$ mho, obtained in experiment (ii), indicates that two months was too short a period for equilibrium to be established. This result, therefore, is discarded. From the mean of the other four results it may be concluded that the final conductivity of the aged suspensions is $70·5\pm1\times10^{-6}$ mho at 20°C.

Kohlrausch and Rose[12] carried out some determinations of the conductivity of saturated magnesium hydroxide solutions. Their values ranged from 93 to 69×10^{-6} mho at 18°C. Taking the temperature coefficient of conductivity to be 2 per cent per degree, and neglecting the temperature coefficient of solubility, their lowest figure corresponds to about 72×10^{-6} mho at 20°C.

In close agreement with this latter result are two values obtained by Le Blanc and Richter[3]. These workers used oxides prepared by igniting magnesium carbonate. In one experiment the final conductivity was $68{\cdot}3\times10^{-6}$ mho at 18°C. after ageing for twenty weeks; in another the conductivity fell from $169{\cdot}3$ to $68{\cdot}92\times10^{-6}$ mho at 18°C. in three weeks. With an oxide prepared by heating magnesium nitrate, however, they found that the conductivity of the suspension fell from $227{\cdot}4$ to $123{\cdot}1\times10^{-6}$ mho, and they concluded that oxides prepared from the nitrate give rise to a higher conductivity. The present investigation does not support this conclusion.

Dupré and Bialas[13] reported a value of $62{\cdot}6\times10^{-6}$ mho at 18°C. for the saturated solution. The actual value obtained was $77{\cdot}82\times10^{-6}$ mho, after long ageing, from which the conductivity of the water used, $15{\cdot}23\times10^{-6}$ mho, was subtracted. In view of the low purity of the water and the uncertainty of the correction, this value is of doubtful validity.

G. Gallin[14] precipitated magnesium hydroxide by adding ammonia to a solutign of the chloride, allowed the solution and precipitate to stand for several days, centrifuged, washed and saturated water of conductivity $4{\cdot}1\times10^{-6}$ mho with the product. The value of the conductivity reported was $50{\cdot}391\times10^{-6}$ mho at 18°C. Carbon dioxide appears to have been excluded only during the saturation of the magnesium hydroxide solution. This result is surprisingly low.

DISCUSSION

(*a*) Solubility of magnesium hydroxide

The concentration of a magnesium hydroxide solution may be calculated from its conductivity, if we assume the solution to be completely dissociated, and the equivalent conductance to be equal to that at infinite dilution. The latter quantity has been taken, from data in the literature, as $228{\cdot}5$ mho at 20°C.

Previous investigators have sometimes reported two solubilities for magnesium hydroxide; one for a metastable or "active" form, the other for the stable form. The results of this investigation do not support the theory that there is any definite solubility which can be assigned to the metastable form, assuming such a form to exist. Thus the maximum conductivities observed in the different experiments range from $135{\cdot}7$ to 181×10^{-6} mho at 20°C. (corresponding to magnesium hydroxide concentrations of $2{\cdot}9$ to $4{\cdot}0\times10^{-4}$ moles per litre), and even different experiments with the samples from the same stock of oxide have resulted in quite different maxima (*cf.* experiments 11 and 12, Table II). The maximum concentration attained is clearly dependent on the relative rates of formation of the hydroxide and of ageing.

The only true solubility of magnesium hydroxide, therefore, is that observed when ageing is complete. This solubility may be calculated from the conductivity reported above for fully-aged suspensions, namely, $70{\cdot}5\times10^{-6}$ mho at 20°C. This gives for the solubility $1{\cdot}52\times10^{-4}$ moles per litre at 20°C.

(*b*) The nature of the ageing process

We may immediately discard the theory of Remy and Kuhlmann[4] that absorption of carbon dioxide brings about the fall in conductivity. In the first place carbon dioxide was excluded both in this investigation and in that of Remy and Kuhlmann, who, however, postulated that this gas diffused into their suspensions through a ground-glass joint. Secondly, magnesium carbonate is considerably more soluble than

magnesium hydroxide, so that absorption of carbon dioxide by a suspension containing excess solid would lead not to a fall but to a rise in conductivity, the increased ionic concentration more than compensating for the lower mobility of the carbonate as opposed to that of the hydroxide ion*.

That hydration of magnesium oxide is the process causing the fall in concentration, as suggested by Le Blanc and Richter[3], is also unlikely. The low temperature coefficient found for the velocity of the ageing process in suspensions prepared from the amalgam rules out any chemical process such as hydration as being the rate-determining process.

Gjaldbaek[5] came to the conclusion that there were two distinct forms of magnesium hydroxide, each with a definite solubility. The present investigation fails to detect any metastable form, since the solutions do not become saturated with respect to any substance of constant solubility except the stable hydroxide. While the non-existence of a distinct metastable form cannot be inferred from this, X-ray studies[7, 8] have shown only one crystal structure for hydroxides of different ages, but indicate an increase in particle size with age.

It would therefore seem probable that the decrease in concentration with time corresponds to the gradual growth of large particles at the expense of small particles of abnormally high solubility. The process would be similar to that of crystallization from a supersaturated solution, also an autocatalytic process[15]. A particle of large size and low solubility will be surrounded by a film of solution of low concentration. Diffusion of dissolved ions into this film will take place from the region of high concentration around the small particles. Crystallization will then occur on the large particles, while the small particles will dissolve. This is the familiar process of recrystallization or Ostwald ripening; but consideration of the mechanism involved makes it clear that increasing the number of large particles will increase the overall rate of the process by increasing the number of regions of low concentration into which diffusion may occur. An acceleration would also be produced by an increase in the size of the large particles already present. This would speed up diffusion by increasing the concentration gradient between large and small particles. Such effects would account for the autocatalytic nature of the process.

It might, however, be pointed out that increase in solubility with decreasing particle size is more marked, the greater the surface energy of the solid considered. A rough measure of the surface energy of a solid is its hardness. Since magnesium hydroxide is soft, having a hardness of only 2 on Moh's scale, it would not be expected to show a very great variation of solubility with particle size. It may well be, therefore, that ageing of the hydroxide involves more than a simple growth of individual crystals. Berger[16], for example, considers that increase of size of primary particles is accompanied by a disgregation of secondary particles into the constituent primary particles.

Similar ageing phenomena have been observed with other metallic hydroxide sols[17]. That of magnesium hydroxide shows the effect to an uncommonly marked extent. The problem is a complex one, and for a full understanding of the processes which take place further information is required. Future investigations might well include studies of the effect on the ageing process of such factors as:—

(i) variations in the heat-treatment of the magnesium oxide used;

(ii) the presence of dissolved salts in the suspension;

(iii) alteration of the solubility of the hydroxide by the addition of alcohol;

(iv) the addition of insufficient oxide (or amalgam) to saturate the solution.

* To make quite certain of this fact, carbon dioxide was passed through a suspension of magnesium hydroxide. As predicted, a considerable rise of conductivity ensued.

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DIE BEPALING VAN SWAWEL IN ORGANIESE VERBINDINGE

deur

T. J. W. JORDEN en H. L. F. SNYMAN

SUMMARY

To replace the Carius method for the determination of sulphur in organic compounds the method described by Elving and Ligett for halogens has been adapted and a satisfactory method evolved for the determination of sulphur in such compounds. Analyses of 13 different compounds representing 7 different structure-types are given.

OPSOMMING

Om die Carius-metode vir die bepaling van swawel in organiese verbindinge te vervang is die metode van Elving en Ligett aangepas en verwerk en is 'n bevredigende metode ontwikkel om die swawel in organiese verbindinge te bepaal. Analises op 13 verskillende verbindinge van 7 verskillende struktuurtipes word aangegee.

Vir die bepaling van swawel in organiese materiaal bestaan daar prinsipiëel tenminste vier metodes, nl:—

(i) Die verbranding van die stof in alkoholiese oplossing en die versameling van die swawel in die verbrandingsgasse in 'n alkaliese oplossing. Hierdie metode word veral gebruik by die bepaling van kleiner konsentrasies swawelhoudende vloeistowwe as onsuiwerhede in ander vloeistowwe, soos bv. die bepaling van tiofeen in benseen.

(ii) Die bekende Eschka-metode waar die stof vermeng word met 'n groot oormaat van 'n mengsel van ligte magnesiumoksied en natriumkarbonaat en dan gegloei word totdat alle organiese materiaal verbrand is. Hierdie metode word veral by die bepaling van swawel in steenkool en kooks gebruik.

(iii) Die verbranding van die stof in 'n verbrandingsbuis by hoër temperatuur in lug of suurstof oor 'n geskikte katalitiese oppervlak soos bv. kwarts, en die versameling van die verbrandingsgasse in 'n alkaliese oplossing. Hierdie metode is taamlik algemeen toepasbaar, maar weens die voorsorgmaatreëls wat dit vereis, het dit tot nogtoe weinig ingang gevind.

(iv) Die bekende en meer klassieke Carius-metode wat in elementêr-analises nog die algemene en bruikbare metode daarstel.

Dit is nie ons doel om hier 'n oorsig te gee van die taamlik lywige literatuur met betrekking tot die bepaling van swawel in organiese materiaal nie. Ons wil ons slegs bepaal by 'n alternatiewe metode om die Carius-metode te vervang en sodoende die nadele verbonde aan die Carius-metode te vermy. Soos bekend is die Carius-metode nie juis elegant nie, is dit waagsaam in gevalle waar monstermateriaal beperk en kosbaar is daar die bepaling mag verongeluk gedurende die verhittingsstadium in die verseëlde buis, en hou dit selfs 'n mate van gevaar in vir die persoon wat die bepaling doen. Die nuwe metode wat ons hier wil beskryf is nie onderhewig aan hierdie nadele nie.

Enige jare gelede is deur Elving en Ligett[1] gevind dat die bekende Lassaigne-toets vir elemente soos stikstof, halogene en swawel in organiese materiaal vatbaar is vir kwantitatiewe verwerking om halogene te bepaal. Hierdie metode van Elving en Ligett vir halogeenbepaling is deur ons uitgetoets en dadelik in gebruik geneem as 'n uitstekende metode in die elementêr-analise vir halogene. Dit het voor die hand gelê dat dieselfde metode ook geskik mag wees vir verwerking vir die kwantitatiewe bepaling van swawel in organiese verbindinge. Pogings in hierdie rigting was uiteindelik suksesvol, en dit is moontlik gevind om organiese swawelverbindinge van verskillende

struktuurtipes in aanraking met gesmelte natriummetaal en natriumdamp volledig te ontbind en om die swawel kwantitatief in anorganiese vorm as natriumsulfied te bind.

Van 'n groot aantal swawelhoudende organiese verbindinge wat reeds met hierdie nuwe metode geanaliseer is gee ons die resultate verkry op die volgende 13 voorbeelde:

Verbinding	*Formule*	*Persent S Gevind*	*Persent S Bereken*
1. *Sulfiede*:			
(*a*) Bis-(2, 4-dinitro-feniel)-sulfied	$C_{12}H_6O_8N_4S$	8·58 8·57	8·70
(*b*) Sisteen	$C_6H_{12}O_4N_2S_2$	26·77 26·64	26·69
2. *Tioureum*:			
m-Nitrofeniel-tioureum	$C_7H_7O_2N_3S$	16·00 15·98	16·27
3. *Tiokarbasiensure*:			
(*a*) ω-Feniel-tio-tiol-karbasiensuur	$C_7H_5N_3S_2$	34·85 34·77	34·78
(*b*) ω-Feniel-tio-tiol-karbasiensuur-bensielester	$C_{14}H_{14}N_2S_2$	23·13 23·07	23·36
(*c*) ω-Feniel-tio-tiol-karbasiensuur-*p*-nitro-bensielester ...	$C_{14}H_{13}O_2N_3S_2$	20·10 20·00	20·06
(*d*) *ω-Feniel-tio-tiol-karbasiensuur-2, 4-dinitro-bensielester	$C_{14}H_{12}O_4N_4S_2$	17·76	17·60
(*e*) *ω-Feniel-tio-tiol-karbasiensuur-*p*-broom-bensielester ...	$C_{14}H_{13}N_2BrS_2$	18·24 18·00	18·15
(*f*) *ω-Feniel-ω-karbanilo-tio-tiol-karbasiensuur-metiel-2, 4-dinitrofeniel-diester	$C_{21}H_{17}O_5N_5S_2$	13·24	13·26
4. *Triasoloon*:			
*1, 4-Difeniel-1, 2, 4-triasoloon-(5)-3-tio-(2, 4-dinitro-benseen)	$C_{20}H_{13}O_5N_5S$	7·28 7·17	7·35
5. *Tiofeen*:			
Tetrafeniel-tiofeen	$C_{28}H_{20}S$	8·28 8·13	8·25
6. *Tiasien*:			
Fenotiasien	$C_{12}H_9NS$	16·10 16·01	16·08
7. *Tritioformaldehied*	$C_3H_6S_3$	69·20 69·68	69·45

* Die beskrywing van hierdie nuwe verbindinge volg elders.

Apparaat en metode

Die analitiese en apparatiewe tegniek, aangepas waar nodig, is in wese dieselfde soos die deur Elving en Ligett voorgeskryf, en is uitgevoer in 'n ontbindingsoond deur ons self ontwerp en in die laboratorium gebou.

Ontbinding van monster deur verhitting

Die reaksiebuis word so vinnig moontlik tot 500°C. verhit en vir een uur by 500°C. gehou. Gewoonweg is dit voordelig om 'n reaksiebuis met 'n lang nek te hê daar so 'n buis meermale gebruik kan word. By vlugtige stowwe, egter, of stowwe wat redelik maklik sublimeer, is dit noodsaaklik dat die nek van die reaksiebuis nie te lank moet wees nie, sodat die hele reaksiebuis tot die gewenste temperatuur verhit kan word. Word hierdie voorsorg nie getref nie is die waardes geneig om te laag te wees.

Verwerking van ontbonde materiaal

Die afgekoelde reaksiebuis word oopgemaak deur eers die inhoud tot lugdruk te bring deur 'n klein gaatjie by die verseëlde punt te smelt, en dan die verseëlde end af te sny. Die oormaat natriummetaal in die buis word dan gebind deur die toevoeging van ca. 10 ml. droë suiwer alkohol. Na beëindiging van die reaksie word die reaksiebuis verhit om seker te maak dat alle natriummetaal verniętig is deur die alkohol, en hierby word dan ca. 10 ml. gedistilleerde water gevoeg om die natriumsoute op te los. Die oplossing word in 'n beker oorgedra, en die reaksiebuis herhaaldelik met warm water uitgespoel. Hierdie oplossing saam met die verkoolde res van die monster en die reste van die monsterbuisie word gefiltreer en die helder filtraat onder toevoeging van 'n verdere een gram natriumhidroksied met broomwater warm geoksideer. Na oksidasie word die oplossing met soutsuur aangesuur, die oormaat broom afgekook en die sulfaat op die gewone manier met bariumkloried neergeslaan, afgefiltreer, gebrand en geweeg. Die bariumsulfaat na verbranding word met een of twee druppels swawelsuur gerook en weer gebrand voordat dit geweeg word.

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DIE SPEKTROCHEMIESE BEPALING VAN BORON IN STAAL

deur

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SUMMARY

A method with D.C. arc excitation is described for the quantitative determination of boron in steel, to a lower limit of ·005 per cent B. The method is reliable and readily applied. A scheme for the semi-quantitative determination of boron in the range ·005–·0006 per cent B is also provided.

OPSOMMING

'n Metode is beskrywe vir die kwantitatiewe bepaling van boron in staal, met opwekking in 'n gelykstroomboog tot 'n laagste konsentrasie van ·005 persent B. Die metode is betroubaar en geredelik uitvoerbaar. 'n Skema word ook aangegee waarvolgens boron-gehaltes van 'n orde kleiner op 'n semi-kwantitatiewe manier bepaal kan word.

As gevolg van die metallurgiese betekenis van klein hoeveelhede boron in staal, en die moeilikhede wat onstaan by die chemiese bepaling daarvan[1], is verskeie spektrochemiese metodes vir hierdie doel ontwikkel[2].

Hierdie metodes berus egter op die foutiewe veronderstelling dat die Boron-gehalte van stale in die gebied ·02 – ·2 persent, of selfs meer sou wees, terwyl latere ondersoek[3] bewys het dat die boron-gehalte gewoonlik meer as 'n orde kleiner is. Om die verhardbaarheid van stale te verhoog is die boron byvoegings gewoonlik minder as ·01 persent, meestal in die gebied ·001 – ·005 persent. Chemiese metodes om boron in sulke klein konsentrasies te bepaal is moeilik en onakkuraat, en die gebrek aan geskikte analitiese metodes was in die verlede 'n stremmende faktor by die ontwikkeling van boron-stale[3].

Die spektrochemiese bepaling van boron in sulke lae konsentrasies lewer ook verskeie moeilikhede op, deurdat daar net twee analiselyne vir boron in die lynryke yster spektrum verskyn. Van hierdie twee word die gevoeligste lyn, B 2497·73, gesteur deur Fe 2497·82. Die ander lyn B 2496·78, lê tussen die Fe-lyne 2496·53 en 2496·99 en 'n spektrograaf met hoë dispersie is dus nodig om hulle te skei indien die spektrumlyne breed genoeg moet wees om gefotometreer te word.

Die National Bureau of Standards van die V.S.A. (N.B.S.) het nogtans gevind dat boron, met behulp van 'n groot Littrow-spektrograaf en die lynpaar B 2496·78/ Fe 2496·99, kwantitatief bepaalbaar is soos volg:—

Elektrodes	*Opwekking*	*Laagste bepaalbare konsentrasie*	*Akkuraatheid*
Twee monsterstafies van 7/32 dm. deursnit.	Wisselstroomboog 2,500 volt. 4 amp.	·0005 persent	Gemiddelde afwyking ± 4 persent vir konsentrasies meer as ·001 persent.
Plat monstervlak teenoor grafiet ...	do.	·003 persent	
do.	Oorgedempte ontlading, A.R.L. Multisource.	·0005 persent	Gemiddelde afwyking ± 4 persent.

Omdat hierdie opwekkingsbronne egter nie algemeen beskikbaar is nie, is die moontlikhede van boron bepaling met behulp van 'n gelykstroomboog ondersoek, en die volgende twee metodes in hierdie Laboratorium uitgewerk.

(*a*) Die bepaling van boron in die gebied ·005 tot ·02 persent

Spektrograaf: Applied Research Laboratories (A.R.L.), Model 2060.

Rooster: Krommingstraal = 1·5 m., 24,000 lyne/duim. Spleetwydte: ·04 mm. Om voldoende dispersie te verkry is die opnames in die tweede orde ultravioletgebied gemaak waar die dispersie 3·5 A°/mm. bedra. Die opnames is gemaak op Kodak S.A. No. 1-emulsie, onder reproduseerbare kondisies ontwikkel, gefotometreer, en die intensiteitsverhoudings van die lynpare met behulp van 'n emulsie-kalibreringskurwe en rekenbord vasgestel.

Elektrodes: Die ondersoek is uitgevoer met die gestandaardiseerde boronstale van die N.B.S. Hierdie standaarde dek die gebied ·0006 – ·019 persent B en is beskikbaar in die vorm van stafies $^1/_2$ duim dik en $^7/_{32}$ duim dik. Voorlopige ondersoek het gewys dat die gebruik van twee stafies van $^7/_{32}$ duim teenoor mekaar ongeskik is. Die verwarming van die anode by die hoë stroomsterkte wat nodig is om die boron te vervlugtig veroorsaak dat daardie elektrode te vinnig wegsmelt. Die beste reproduseerbaarheid is verkry met 'n $^1/_2$ duim-staaf effens rondgeslyp, as anode, en daarteenoor 'n $^7/_{32}$ duim-staaf konies afgeslyp na 'n 80°-punt, as katode. Die elektrodes is vars afgeslyp voor elke opname.

Opwekking: Met 'n gelykstroomboog van 6 ampere en 'n booglengte van 3 mm., vorm daar na 'n brandtyd van 5 sek. 'n gloeiende krater op die anode, wat verhoed dat die ontlading willekeurig op die anode rondbeweeg. Hierdie lokalisering van die brandvlek is bevorderend vir die gevoeligheid van die bepaling. Opnames met en sonder voorbrand het aangetoon dat 'n voorbrandtyd van 5 sek. gewens is, gevolg deur 'n beligting van 15 sek.

Werkskurwe: Die beste reproduseerbaarheid is verkry met die lynpaar B 2496·78/Fe 2496·53 (Tabel I), en 'n werkskurwe opgestel vir die konsentrasiegebied ·005 – ·02 persent B. Vir hierdie konsentrasiegebied verander die intensiteitsverhouding B/Fe van ·3 – ·9, en kan die lynpaar dus gebruik word om boron tot kons. van ± ·05 persent, waarvoor die intensiteitsverhouding ±1·6 bedra, te bepaal.

TABEL I

Reproduseerbaarheid van fotometreerde lynintensiteite

N.B.S. monster 828 *persent B*=0·0059				*N.B.S. monster* 829 *persent B*=0·0091			
Opname	*Persent transmissie*		*Intensiteits-ver. B/Fe*	*Opname*	*Persent transmissie*		*Intensiteits-ver. B/Fe*
	Fe 2496·53	*B* 2496·78			*Fe* 2496·53	*B* 2496·78	
1	17·4	67·0	·33	1	12·9	41·2	·46
2	11·4	57·0	·31	2	6·8	23·4	·46
3	22·2	74·6	·32	3	17·4	51·4	·46
4	8·4	46·3	·32	4	12·6	42·6	·44
5	12·8	59·5	·32	5	7·6	26·1	·46
6	12·4	58·7	·32	6	13·4	43·4	·45
7	15·0	65·6	·31	7	7·3	26·0	·46

Omdat B 2496·78 betreklik ongevoelig is en die agtergrond-intensiteit steurend word was fotometrering van die B-lyn by hier konsentrasies nie moontlik nie. Vir die gebied ·005 – 02 persent is die werkskurwe egter betroubaar en wys die resultate 'n standaard afwyking van ± 3 persent van die totale borongehalte.

(*b*) Die semi-kwantitatiewe bepaling van boron in die gebied ·0006 – ·005 persent

Deur die spektrograafspleet te verklein na ·01 mm. kan die gevoelige lyn B 2497·73 bevredigend van die naburige Fe-lyne geskei word. Omdat die lyn dan te smal is om gefotometreer te word, word die intensiteit daarvan met die oog vergelyk met die van geskikte Fe-lyne volgens die skema van Tabel II. In hierdie tabel word die volgende afkortings gebruik:

B 2496·78=B_1	Fe 2498·21=Fe_1
B 2497·73=B_2	Fe 2496·07=Fe_2
	Fe 2497·30=Fe_3
	Fe 2497·82=Fe_4
	Fe 2496·53=Fe_5

TABEL II

Skema vir die semi-kwantitatiewe bepaling van B in lae konsentrasies

N.B.S. monster	*Persent B*	*Vergelyking van B_1 met Fe-lyne*	*Vergelyking van B_2 met Fe-lyne*
425	·0006	B_1 onsigbaar	$B_2 < Fe_1 < Fe_2$
426	·0011	B_1 net sigbaar $< Fe_1 < Fe_2$	$B_2 \simeq Fe_1 < Fe_2$
427	·0027	$B_1 \simeq Fe_1 < Fe_2$	$Fe_1 < B_2 \simeq Fe_2 < Fe_3$
428	·0059	$Fe_1 < B_1 < Fe_2 < Fe_3$	$Fe_2 < B_2 \simeq Fe_3 < Fe_4$
429	·0091	$Fe_1 < B_1 \sim Fe_2 < Fe_3$	$Fe_3 < B_2 \simeq Fe_4 < Fe_5$
430	·019	$Fe_3 < B_1 < Fe_4$	$Fe_4 < B_2 \simeq Fe_5$

Tabel II wys ook hoedat hierdie semi-kwantitatiewe skema uitgebrei kan word om borongehaltes tot ·02 persent te omvat.

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THE HYDROXYL VALUE OF FATTY COMPOUNDS

by

FRANK HAWKE

OPSOMMING

Daar is gevind dat die asynsuuranhidried-piridien metode vir die bepaling van hidroxiel-groepe onbestendige resultate gee. Eksperimente is uitgevoer om die invloed van die volgende faktore te bepaal: suiwerheid van die reagense; aanwesigheid van 'n klein hoeveelheid water in die asetileringsreagens; effek van konsentrasie van daardie reagens op die oormaat wat nodig is om kwantitatiewe asetilering te verseker; tyd en temperatuur vir hidrolise van die oormaat asynsuuranhidried; en die metode wat gebruik is om die vry-suurgraad te bepaal. 'n Matematiese ontleding van die metode word ingesluit om die invloed van verskeie faktore op die juistheid van die metode aan te toon.

As gevolg van hierdie ondersoek word 'n gewysigde metode aanbeveel, en analitiese data word verskaf om die toepasbaarheid daarvan te illustreer.

SUMMARY

The pyridine-acetic anhydride method for the determination of hydroxyl groups was found to give erratic results. Experiments were carried out to determine the effects of the following factors: purity of the reagents; the presence of a small amount of water in the acetylating reagent; the concentration of that reagent on the excess necessary to ensure quantitative acetylation; the time and temperature of the hydrolysis of the excess acetic anhydride; and the method used for the determination of the free acidity. A mathematical analysis of the method is included to show the influence of several factors on the precision of the method.

As a result of these investigations a modified method is proposed and analytical data are presented to illustrate its applicability.

The assessment of the purity of hydroxy-fatty acids and their esters depends very largely upon the determination of their hydroxyl values and the following investigation was undertaken to develop a reliable, precise and accurate method for this determination.

Of the various procedures in use today, the André-Cook[1, 2] has attained the status of a standard method, but suffers from two main drawbacks: it is inapplicable to free fatty acids owing to the formation of relatively stable mixed anhydrides[3], while the prolonged boiling of the acetylated product with water may lead to partial hydrolysis, thus giving low results[4]. The modification of Roberts and Schuette[4], in which the acetylated product is not isolated, eliminates hydrolysis of the acetyl derivative, but does not, in the present author's opinion, obviate the possibility of the formation of mixed anhydrides with free fatty acids.

The remaining procedures are largely those based on acetylation with acetic anhydride in pyridine solution, originally suggested by Verley and Bölsing[5]. These methods appear to be free from the major defects of the procedures in which acetic anhydride is used alone, and it was decided to investigate them more fully.

The methods are all based on the reaction $R.OH+(CH_3CO)_2O+C_5H_5N = R.OCOCH_3 + CH_3COOH.NC_5H_5$, and consist, in essence, of acetylating the material with a solution of acetic anhydride in pyridine, hydrolysing the excess acetic anhydride and back-titrating the acetic acid formed either with or without homogenization with *n*-butanol.

Experimental work was begun using the British Ministry of Supply method[6], but this was found to give erratic results, even when the sample weight was reduced to 0·5 gram. A survey of the literature showed that, although a number of factors had been investigated[7, 8], the methods published to date were not completely reliable, since subsequent workers were unable to obtain satisfactory results without modifying the methods[9, 10]. This study of published methods also revealed that the majority of them were of relatively low precision, or else involved the use of special apparatus[11].

The material used in this investigation (except where otherwise stated) was a sample of crude methyl ricinoleate of about 91 per cent purity and containing a small amount of œnanthaldehyde. It had an acid value of 1·44 mg. KOH per gram and an hydroxyl value of 161·2 mg. KOH per gram. For the hydrolysis tests castor oil fatty acids were also used, having an acid value of 165·6 mg. KOH per gram and an hydroxyl value of 152·5 mg. KOH per gram.

Acetic anhydride-pyridine reagent

Preliminary experiments were carried out using freshly-distilled medicinal grade pyridine (B.R. 108 – 108·5°C., 620 mm.Hg.) previously dried over KOH for at least 48 hours, and freshly-distilled reagent grade acetic anhydride (B.R. 132·2 – 132·7°C., 620 mm.Hg.). The reagent was prepared by adding one volume of acetic anhydride to nine volumes of pyridine, but it was found that results were erratic, even when using freshly-prepared reagent.

This confirmed the findings of Wilson and Hughes[7], who showed that the presence of less than 0·3 per cent or more than 0·5 per cent of water in the reagent caused low and unreliable results. These authors suggested that the presence of 0·3 to 0·5 per cent. of water, while in no way interfering with the acetylation of the hydroxy compound, inhibits the reaction between acetic anhydride and pyridine at temperatures below 100°C. The occurrence of this latter reaction in the absence of water can be observed by the darkening of the reagent in the blank determination. Since it is most probable that this reaction is influenced by the concentration of acetic anhydride, the error introduced in the blank will differ from that in an actual determination with the result that erratic results will be obtained in the complete absence of water.

In order to ensure that neither the acetic anhydride nor the pyridine absorbed water from the atmosphere after distillation, it was decided to seal these reagents in separate ampoules immediately after purification, the contents of each ampoule being sufficient for a duplicate determination.

Concentration and excess of reagent

Having obtained a reagent of satisfactory purity and water content, experiments were carried out to study the influence of the concentration of acetic anhydride on the excess necessary for quantitative acetylation.

The most dilute solution used consisted of one volume of acetic anhydride in nine volumes of pyridine (1 : 9). This reagent is perfectly satisfactory provided a sufficiently large excess is used. Increase in concentration of acetic anhydride results in a lowering of the excess necessary for complete acetylation, but the present author did not use solutions more concentrated than 1 : 3 since this would require the use of specialized apparatus for measuring out the small volume of reagent necessary.

The effects of concentration on excess of reagent necessary are shown in Table I.

It will be seen from Table I that, whereas a reagent containing only 10 per cent of acetic anhydride requires a molar excess of the order of two, one containing twenty-five per cent of acetic anhydride gives quantitative results with a molar excess of only one. An important corollary to this is that by reducing the excess the precision is improved considerably.

The use of too great an excess of reagent (about 5 mols. per mol. reacted) tended to give erratic results, several units high. In such cases a slight darkening of the ester was noticeable and it was assumed to be due to the reaction between the acetic anhydride and œnanthaldehyde. This was confirmed by the results obtained when using a five molar excess on castor oil, free from aldehydes (Table II).

TABLE I

Conc. of reagent	*Sample weight (grams)*	*Molar excess of Ac_2O*	*Hydroxyl value*	*"Precision"**
1:9	2·8922	0·13	151·8	0·10
	2·2008	0·49	157·1	0·13
	1·0005	2·25	161·2	0·29
1:4	1·3277	1·44	160·8	0·20
	1·1339	1·85	161·2	0·21
	1·0028	2·22	161·5	0·24
1:3	2·0786	0·99	161·2	0·15
	2·0340	1·05	161·6	0·15
	1·9645	1·10	161·3	0·16

* The term "precision" is defined as the change in hydroxyl value caused by a variation in titre of 0·01 ml. of alkali. (*See* mathematical analysis.)

TABLE II

Material	*Molar excess of Ac_2O*	*Hydroxyl value*
Methyl ricinoleate ...	5·03	165·1
	5·50	162·9
Castor oil	5·01	163·8
	4·97	164·2
	1·13	163·9

Time of acetylation

The time required for complete acetylation varies with temperature, but an upper temperature limit is set by the fact that above 100°C. water ceases to have an appreciable inhibitory effect on the reaction between acetic anhydride and pyridine[7].

In order to keep the time of acetylation to a minimum while maintaining the inhibitory effect of 0·4 per cent of water, it was decided to acetylate on a boiling water bath. Using a one molar excess of acetic anhydride (in the form of a 1: 3 solution), reliable results were obtained with two hours acetylation, but reduction of this time to three-quarters of an hour or even an hour resulted in incomplete acetylation, as shown in Table III.

TABLE III

Time of acetylation (hours)	*Molar excess of Ac_2O*	*Hydroxyl value*
¾	1·05	156·4
1	1·04	157·2
2	1·05	161·6

Conditions of hydrolysis of excess acetic anhydride

A study of the literature revealed a large number of techniques for hydrolysing the excess acetic anhydride, these varying from pouring the contents of the acetylation

flask into ice water[12] to heating on a boiling water bath for 15 minutes[6, 11] or even longer[9]. Since incomplete hydrolysis leads to high results, while excessive reaction with water is liable to hydrolyse the acetyl derivative, systematic experiments were carried out to determine the optimum hydrolysis conditions.

In order to stabilize other variables, the hydrolysis experiments were performed on aliquots of a solution made up by diluting the product of a bulk acetylation with dry pyridine.

Preliminary experiments showed that 10 ml. of ice water required 2 minutes to hydrolyse 5 ml. of 1:3 reagent and hence no subsequent experiments were carried out at temperatures below 20°C.

TABLE IV

Material acetylated	*Hydrolysis at room temperature*		*Hydrolysis on boiling water bath*	
	Time (minutes)	*Hydroxyl value*	*Time (minutes)*	*Hydroxyl value*
Methyl ricinoleate ...	1	166·9; 161·9	2	161·3
			15	161·3; 161·4
			30	160·4
Castor oil fatty acids ...	1	214·8; 209·0	15	152·9; 152·7

From Table IV it can be seen that 15 minutes' hydrolysis on a boiling water bath gives the most reliable results and also that the excess acetic anhydride is less readily hydrolysed in the presence of castor oil fatty acids than in the presence of methyl ricinoleate.

Alkali solution used for back-titration

Experiments showed that no advantage was gained by the use of methyl alcoholic alkali. Hence it was decided to use ethyl alcoholic KOH made up as described by Jamieson[13]. This solution is free from aldehydes and remains colourless for several months. Although it may be kept for a week in a tightly stoppered bottle without appreciable change in titre, it is advisable to standardize the alkali daily.

The concentration of 0·55 N was selected to give a blank titration of about 48 ml., thereby using a 50 ml. burette to the best advantage.

Indicator

The sharpness of the end point was found to be much improved by the use of a cresol red-thymol blue mixed indicator, similar to that recommended by Kleinzeller and Trim[14], but made up in ethyl alcohol.

Determination of acidity

Methods for determining free acidity of the sample vary from repeating the complete hydroxyl value procedure, using pyridine instead of acetylation reagent[3, 11], to determining it by one of the standard acid value techniques[6].

The results of experiments to determine the effect of method on the acid value of castor oil fatty acids are shown in Table V.

TABLE V

Method	*Acid value (mg. KOH/gram)*
Exactly as hydroxyl value, but using pyridine in place of acetylation reagent.	165·8; 165·3 Mean: 165·6
Sample + 5 ml. pyridine + 75 ml. neutral *n*-butanol, titrated at room temperature.	165·7; 165·4 Mean: 165·6
Sample + 50 ml. hot, neutral ethyl alcohol, titrated hot.	165·2; 165·0 Mean: 165·1

From this it can be seen that the standard acid value method gives results slightly lower than the other two methods. This is probably due to the fact that the standard method involves the titration of a hot solution.

Precision of method

It was decided to carry out a mathematical analysis of the precision of the various methods, based on the primary assumption that the end point of a titration can be judged with a precision of 0·01 ml.[15].

The hydroxyl value is defined as the number of milligrams of KOH equivalent to the acetic acid liberated on the complete hydrolysis of the acetylated product obtained from one gram of material.

The following calculations are based on the use of a neutral fat of hydroxyl value 165, the titration figures being computed from this value, together with the published concentrations of reagent and alkali. The molar concentrations of acetic anhydride are calculated from the volumetric concentration of the reagent, neglecting the contraction in volume on mixing (found to be 0·5 per cent in the case of the 1 : 3 reagent)

If A ml. of acetic anhydride is mixed with P ml. of pyridine, the molar concentration of acetic anhydride will be $\frac{1\cdot082A}{102\ (A+P)}$ mols. per ml., where 1·082 is the density of acetic anhydride and 102 its molecular weight. This expression reduces to:

$$\frac{10\cdot6A}{A+P} \text{ millimols. } Ac_2O \text{ per ml.} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Let V_b ml. of F normal alkali be equivalent to V_r ml. of acetylating reagent. Then,

$$V_b = \frac{(2)\ (10\cdot6)AV_r}{(A+P)F} \text{ (since } (CH_3CO)_2O \equiv 2CH_3COOH) \quad \ldots\ldots\ldots\ldots \quad (2)$$

$$= \frac{21\cdot2AV_r}{(A+P)F} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2a)$$

The volume of alkali (V_s) equivalent to the acetic anhydride used to acetylate W grams of material of hydroxyl value H can be derived as follows:

W grams material ≡ WH mg. KOH (by definition)

$$= \frac{WH}{56\cdot1} \text{ milli-equivs. KOH} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$= \frac{WH}{56\cdot1F} \text{ ml. F normal KOH,}$$

$$\text{or,}\quad V_s = \frac{WH}{56{\cdot}1F} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3a)$$

The molar excess (X) of acetic anhydride can now readily be calculated from the expression—

$$X = \frac{\dfrac{10{\cdot}6AV_r}{A+P} - \dfrac{WH}{56{\cdot}1}}{\dfrac{WH}{56{\cdot}1}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

(The milli-equivalents of KOH equal the millimols of acetic anhydride used, since ROH ≡ $(CH_3CO)_2O$.)

Finally, since the hydroxyl value, H, is calculated from the expression $H = \dfrac{56{\cdot}1(FV_s)}{W}$, the change in hydroxyl value, $\triangle H$, caused by a variation of 0·01 ml. in V_s will be—

$$\triangle H = \frac{56{\cdot}1(F)(0{\cdot}01)}{W}$$

$$= \frac{0{\cdot}561F}{W} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

From equation (5) it follows that the precision of the method increases with increase in sample weight and with decrease in normality of alkali. There is, of course, a number of practical limitations to the values selected for F and W, such as, for example, the minimum permissible excess of acetic anhydride.

The method proposed is based on the use of 5 ml. of 1:3 reagent, thus necessitating a value of 0·55 for F to keep the blank titration within the range of a 50 ml. burette. Since the use of 1:3 reagent requires the use of one molar excess of acetic anhydride, $W_{max.}$ is fixed at a value of about 2 grams.

Data for five published methods, together with those for the proposed method, are given in Table VI.

TABLE VI

Method	*Conc. of reagent*	V_r	*F.*	*Sample wt. (grams)*	V_b	V_s	*X*	$\triangle H$
1[12]	1:3	2	0·5	1·0	21·2	5·89	0·72	0·28
2[9]	1:7	5	0·3	0·34*	44·2	3·43	5·14	0·48
3[11]	1:7	5	0·5	0·5–1·0	26·5	2·94–5·88	3·3–1·15	0·56–0·28
4[7]	1:9	50	1·0	1·0	106	2·94	16·2	0·56
5[10]	1:3	3	0·5	0·3–0·75	31·8	1·76–4·4	7·6–2·4	0·94–0·38
6	1:3	5	0·55	1·5–2·0	48·2	8·0–10·67	1·9–1·1	0·21–0·15

Conc. of reagent represents volumes acetic anhydride: volumes pyridine; V_b, Eqn. (2); V_s, Eqn. (3*a*); X, Eqn. (4); $\triangle H$, Eqn. (5).

* Although the authors recommend the use of 0·5–1·0 gram samples, they used 0·33–0·35 gram in the case of ricinoleic acid.

Method

Reagents

Acetic anhydride: Reagent grade, freshly distilled (B.R. 132·2 – 132·7°C., 620 mm.Hg., corresponding to 139 – 139·5°C., 760 mm.Hg.[16]) and sealed in ampoules, each containing 6 ml.

Pyridine: Medicinal grade, purified for 48 hours over 5 per cent each of ceric sulphate and potassium carbonate, filtered and distilled (B.R. 108 – 108·5°C., 620 mm.Hg., corresponding to 114·8 – 115·3°C., 760 mm.Hg.[17]). Immediately after distillation, 0·4 per cent (by volume) of water is added and the pyridine sealed in ampoules, each containing 18 ml.

Acetylating reagent: This is prepared half an hour before use (to allow it to attain room temperature) by adding the contents of an ampoule of acetic anhydride to those of an ampoule of pyridine in a glass-stoppered bottle and mixing well. (These quantities make sufficient reagent for two determinations and two blanks.).

Indicator: 1 volume of 0·1 per cent alcoholic solution of cresol red, mixed with 3 volumes of 0·1 per cent alcoholic solution of thymol blue.

n-Butanol: Ordinary commercial grade, containing 5 ml. of mixed indicator per litre and neutralized immediately before use.

Alcoholic KOH: 0·55 N. 38 grams of KOH (C.P., pellets) is ground in a mortar with 33 grams of CaO (C.P., lumps). The mixture is then transferred to a flask and well shaken with 1 litre of 94 per cent ethyl alcohol. After standing overnight, the solution is filtered and standardized against standard, semi-normal hydrochloric acid using mixed indicator.

Procedure

(1) *Acetylation*

The sample (1·5 to 2 grams in the case of materials with high hydroxyl values and 4 to 5 grams in the case of materials with low hydroxyl values) is accurately weighed into a 250 ml. flask, fitted with a reflux condenser by means of a ground glass joint. 5 ml. of reagent is then added from a pipette, the condenser fitted to the flask and the flask heated under reflux on a boiling water bath for two hours.

At the end of this period 10 ml. of distilled water is added down the condenser, the contents of the flask are swirled thoroughly and the flask and its contents left on the boiling water bath for a further 15 minutes. The flask is then removed and cooled in water, 50 ml. of neutral butanol containing indicator being added down the condenser during cooling.

When the contents of the flask are cold, it is removed from the cooling water and the tip of the condenser and the neck of the flask washed down with a further 25 ml. of neutral butanol. The contents of the flask are then titrated with standard 0·55 N. alcoholic KOH.

A blank determination is carried out on 5 ml. of reagent alone, under identical conditions.

(2) *Acidity*

This is determined on a similar weight of material dissolved in 5·0 ml. of pyridine to which has been added 75 ml. of neutral butanol containing indicator.

In the case of substances of low acidity, this determination is best carried out using decinormal alcoholic KOH.

(3) *Calculation*

The hydroxyl value is given by the expression—

$$H = 56{\cdot}1\left[\frac{(V_b - V_h)F_h}{W_h} + \frac{V_aF_a}{W_a}\right]$$

where: V_b is the titre of the blank,

V_h and V_a the titres in the hydroxyl and acidity determinations respectively,

F_h and F_a the normality of the KOH used for the hydroxyl and acidity determinations respectively,

and W_h and W_a the weights of sample used in the hydroxyl and acidity determinations respectively.

In Table VII are given the results of hydroxyl value determinations carried out on fatty materials varying in hydroxyl value, acidity and colour. These illustrate the suitability of the method for both research and routine purposes.

TABLE VII

Material	*Range of sample weight (grams)*	*Colour*	*Acid value (mg. KOH/gram)*	*Hydroxyl Value*
Castor oil	1·9–2·0	Pale yellow	4·58	164·0 163·8 163·9 164·1
Methyl ricinoleate	1·9–2·1	Pale yellow	1·44	161·2 161·6 161·2 161·3
Castor oil fatty acids	1·8–2·0	Yellow	165·6	152·7 152·2 152·9 152·1
Cape berry wax	2·6–4·4	Greenish	4·05	71·8 72·1
Dehydrated methyl ricinoleate ...	4·9–5·1	Dark brown	29·9	56·6 57·2
Tung oil	5·0–5·2	Brown	15·4	35·1 35·3
Linseed oil (raw)	5·0–5·2	Light brown	3·86	6·06 6·26

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CHEMICAL TECHNOLOGY OF SOUPFIN-SHARK LIVER OIL

PART II. THE EFFECTS OF STORAGE CONDITIONS ON STABILITY

by

A. W. LATEGAN

OPSOMMING

Eksperimentele data word verstrek om die nadelige effek van verskeie faktore op die stabiliteit van haailewerolie aan te toon. As maatstaf dien die vernietiging van vitamien A sowel as afname in Induksie Periode (I.P.).

Al die gewone metale veroorsaak 'n aansienlike afname in I.P., en vernietig binne drie maande al die natuurlike anti-oksideermiddels in die olie, terwyl die vitamieninhoud met 16–88 persent afneem in nege maande. Koper, geelkoper en lood is relatief gesproke baie nadeliger, terwyl tin en sink minder aktief is. Die pro-oksiderende effek van koper kannie teëgewerk word deur byvoeging van anti-oksideermiddels nie, en koper kan ook nie ongeaktiveer word deur 0·1 persent kupron by olie te voeg wat slegs 5 parte per miljoen koper bevat nie.

Die stabiliteit van lewerolie word tot 'n groot mate bepaal deur die metode en graad van preservering van lewer voordat die olie afgeskei word. Preservering met formalien en boraks verseker relatief hoër stabiliteite. Opberging by lae temperatuur, sonder bewaarmiddel, is onvoldoende. Die I.P. van olie uit lewer wat behoorlik gepreserveer was, verminder met ongeveer 25 persent gedurende opberging vir 'n jaar, terwyl die vitamien A met 5 persent afneem gedurende dieselfde periode. Olie uit lewer wat óf gladnie óf onbehoorlik gepreserveer word, verloor binne drie maande alle weerstand teen oksidasie.

Alle raffinasie-metodes verminder die I.P. met 40–50 persent, en daarna neem dit met nog 25–100 persent af gedurende opberging vir 'n jaar. Raffinasie met alkali is minder skadelik, terwyl koolstof-behandeling die nadeligste is.

Opgeloste lug verminder die I.P. met 40–50 persent, en vitamieninhoud met 10–12 persent gedurende opberging vir 'n jaar, terwyl 'n onaktiewe atmosfeer (CO_2, N_2) hierdie verliese na $\pm$20 persent en $\pm$9 persent respektiewelik verminder.

In 'n oorsig van die literatuur word die invloed van lig aangetoon. Vog versnel die vernietiging van natuurlike anti-oksideermiddels en dit is raadsaam om lewerolie droog te maak sodat dit hoogstens 0·01 persent water bevat.

Hierdie resultate dui aan dat vislewer teen lig moet beskerm, en behoorlik gepreserveer word voordat die olie afgeskei word. Ekstraksie en raffinasie moet sorgvuldig uitgevoer word; metaaloppervlaktes (van houers en apparaat) moet vertin of gegalvaniseer word; die olie moet behoorlik drooggemaak, en in 'n onaktiewe atmosfeer opgeberg word, nadat geskikte antioksideermiddels bygevoeg is.

SUMMARY

The results of spot and storage tests illustrate the adverse effect of several factors and conditions on the stability of shark liver oil. Destruction of vitamin A, and decrease in Induction Period (I.P.), which is a measure of susceptibility to oxidation, are accepted as criteria.

Most metals cause a serious lowering of stability, destroying all natural inhibitors in the oil in about 3 months, while the vitamin A content drops by 16–88 per cent in 9 months. Copper, brass and lead are comparatively much more harmful, while tin and zinc are less active. The pro-oxidative effect of copper cannot be counteracted by the incorporation of anti-oxidants, nor could copper be inactivated by adding 0·1 per cent cupron to an oil containing 5 parts per million copper.

Degree and mode of preservation of liver prior to oil extraction have a very important bearing on stability of extracted oil. Liver samples preserved in formalin or borax yield oil with relatively high storage stability; low temperature storage, without preservative, is not effective. Oil from fresh or well-preserved liver loses about 5 per cent of its vitamin A during storage for 1 year, while the Induction Period decreases by 25 per cent. Unpreserved or insufficiently preserved liver yields an oil which is fully susceptible to oxidation within 3 months.

All refining methods lower Induction Period by 40–50 per cent and during subsequent storage for 12 months a further decrease of 25–100 per cent takes place. Alkali refining is least, and carbon decolorizing most destructive.

Dissolved air causes I.P. to decrease by 40–50 per cent and vitamin A by 10–12 per cent during storage for 1 year, while inert atmospheres (CO_2, N_2) reduce these figures to $\pm$20 per cent and $\pm$9 per cent respectively.

A review of the literature indicates the influence of light. Moisture is shown to promote the destruction of natural inhibitors and it is advantageous to dry liver oil to a moisture content of 0·01 per cent.

The results indicate that fish liver should be preserved well and protected from light prior to extraction of the oil. Care should be exercised as to methods of extraction and refining; all metal surfaces (plant and containers) should be tinned or galvanized; the oil should be dried very well and stored in an inert atmosphere after the incorporation of suitable antioxidants.

Effect of materials of construction of processing plant and containers

Materials of construction of plant and containers usually have an adverse effect on the stability of vitamin A oils. All metals may be regarded as oxidation accelerators, which reduce the stability of oils to varying degrees.

Royce[1] describes the pro-oxidative effect of copper. A review by Lea[2] indicates the activity of one part copper in ten million, which increased the rate of oxidation in herring oil 2½ times. Iron, present in ten times this quantity, was only half as active. Ziels and Schmidt[3] report that all metals tested had a marked pro-oxidative effect, except aluminium and nickel (on hydrogenated cottonseed oil). Lead, manganese, copper, cobalt and iron were most active. These authors suggest a mechanism of reaction whereby metallic soaps are formed by interaction of the metal with free fatty acid present in the fat.

The little information available on the effect of metals on rate of oxidation is widely scattered, and no evidence could be found that fish liver oils, and the rate of destruction of vitamin A have ever been fully investigated. It was therefore decided to determine the effect of various metals on induction period of a fresh shark liver oil, and to store the oil in contact with these metals, and determine the rate of decrease of induction period and vitamin A potency.

The oil was obtained by collecting fresh livers in a wooden box, and extracting the oil from these as quickly as possible, using glass containers only. In this way a good fresh oil, that had not been in contact with metals, was obtained.

Aliquots of this sample of oil were aerated in contact with strips of well-cleaned metal, and stored in contact with metal, while induction period (rapid oxidation method[29, 30, 31]) and vitamin A potency ($E_{1cm.}^{1\ per\ cent}$ 328 mμ—colorimetric method[27, 28]) were determined at regular intervals. A small head-space of air was left in each container, including the control, in order to simulate practical storage conditions.

The following metals, normally used in plant or container construction, or used for making instruments employed in the production of liver oils, were tested:—Mild steel, two types of stainless steel commonly used, *viz.*, chrome steel and chrome-nickel steel, galvanized iron, aluminium, lead, copper, brass and tin. At the same time the effect of rubber was investigated, as rubber piping is invariably used, and the effect of traces of old oxidized oil, to compare the effect of oxidized oil with that of metallic pro-oxidants, and to confirm earlier reports[4, 5] that oxidized oil catalyses the destruction of vitamin A in fresh oils.

In all cases the ratio oil to metal was 250 ml. to 8 sq. inches, which corresponds more or less with the ratio encountered in storage. The metal strips were cleaned very well by scraping and acid pickling and were then dried after rinsing in acetone. Aerations were done at 100°C. and induction period measured to a point when the peroxide value (P.V.) exceeded 25 (ml. 0·002 N. sodium thiosulphate per gram of oil).

A preliminary aeration was carried out in the presence of copper and tin, which were expected to be the most active and least active metals respectively, in order to ascertain whether the previously established relationship between destruction of vitamin A and development of peroxide applies also in the presence of pro-oxidants. The results are given in Table I.

TABLE I

Decrease of $E_{1\ cm.}^{1\ per\ cent}$ 328 *mμ and development of peroxides (P.V.) in liver oil aerated at 100° C. in presence of copper and tin.*

Time (hours)	*Samples*					
	Substrate A		*A plus copper*		*A plus tin*	
	P.V.	$E_{1\ cm.}^{1\ per\ cent}$ 328 *mμ*	*P.V.*	$E_{1\ cm.}^{1\ per\ cent}$ 328 *mμ*	*P.V.*	$E_{1\ cm.}^{1\ per\ cent}$ 328 *mμ*
0	—	5·35	—	5·35	—	5·35
0·5	—	—	23·6	3·1	5·35	—
1	5·72	4·88	37·6	1·83	9·17	4·86
2	9·9	4·36	—	—	26	3·41
2·5	—	—	—	—	75·7	1·46
3	19·8	4·22	—	—	—	—
3·5	38·7	2·39	—	—	—	—

From these results it appears that the same relationship holds, and that vitamin A is rapidly destroyed after the end of the induction period (P.V.=25) is reached.

The storage test, originally planned to run for one year, was stopped after nine months, as it was quite clear, even after six months' storage, that all natural inhibitors had been completely destroyed. In fact, the induction periods are so low after three months that the oils may be then considered fully susceptible to rapid oxidation. It should be pointed out that aeration of stored samples was not done in contact with the metal. The oil had therefore only been in contact with metal at room temperature. The rapid destruction of natural resistance to oxidation becomes even more significant if one considers that most of these samples had induction periods of 1 – 2 hours when aerated originally *in the presence of metals*, and that these induction periods decreased to 0·7 hours or less, when aerated out of contact with metals, after three months' storage.

If one considers the loss of vitamin A (Table II) the figures become even more significant. Over a period of nine months, there is a drop in $E_{1\ cm.}^{1\ per\ cent}$ 328 mμ ranging from 16 – 88 per cent, while the control, stored under identical conditions, but not in contact with a metal, lost only 2·8 per cent. Incidentally, this is the lowest storage loss recorded in the present investigation, and can probably be explained by the fact that this oil was particularly fresh and pure, having been obtained from fresh liver and kept out of contact with all metals.

The spot and storage results are summarized in Table II. Spot aerations were carried out in the presence of metals, while the stored samples were aerated out of contact with metals.

From these figures it would appear that all metals cause a very significant increase in susceptibility to oxidation. In decreasing order of activity (considering induction periods obtained), the metals are arranged as follows:

Copper, brass, rusted mild steel, lead, chrome nickel steel, chrome steel, galvanized iron, aluminium, tin, polished mild steel.

Rubber comes after polished mild steel, but it should be noted that rubber reduced the induction period from 3·2 to 2·6 hours. Polished mild steel appears to exhibit less activity than tin or aluminium, but the sample that had been corroded and then cleaned well, was much more active. This phenomenon will probably be encountered with all metals once corrosion has begun to destroy the smooth surface. The pro-

oxidative activity of the stainless steels is surprising, as one would naturally expect them to be less active than mild steel. Yet the same effect has been reported by King *et al*[6].

Furthermore, it should be noted that 1 per cent of old oil (No. 18) acted pro-catalytically, being superseded only by copper, brass, rusted steel and lead.

In samples 13 and 14 an attempt was made to counteract the pro-oxidative effect of copper by adding citric acid as anti-oxidant. While this was reasonably successful in sample 13 where the oil was aerated in contact with metallic copper, it failed in experiment 14, probably due to the greater activity of copper in the form of cuprous chloride.

The same phenomenon was noticed in samples 15 and 16, where cupron appeared to take up the copper ions formed in the sample containing metallic copper, but could not counteract the pro-oxidative effect of copper when present as a salt. Note that the sample contained only 5 parts copper per million and a very large excess (0·1 per cent.) cupron. Cupron itself did not materially affect the normal induction period (No. 17).

The great activity of copper, whether present in metallic form or as a salt, agrees with the results[6] illustrating the pro-catalytic effect of copper on lard.

In Fig. 1, a graphical illustration is given of the shortening of induction period when the oil is aerated in contact with copper, lead, tin and new mild steel (black iron), as well as a curve to indicate the very rapid rate of peroxide development after three months' storage in contact with copper. It is quite obvious from the latter curve that all resistance to oxidation had been destroyed.

If the metals are now arranged in decreasing order of activity (on the basis of per cent. vitamin A destroyed during storage) the following grading is obtained —

> Copper, lead, chrome steel, aluminium, mild steel, chrome nickel steel, galvanized iron, tin.

While this order differs from that obtained by considering the decrease in induction period, certain features are common to both. Copper, lead and chrome steel are the most active oxidation accelerators, while tin and galvanized iron are least active. Aluminium, while not causing a very serious lowering of induction period during aeration, appears to be an active and direct pro-oxidant for vitamin A.

On the whole, the serious losses of vitamin A appear to present an exaggerated picture of the influence of metals on the stability of the vitamin. These results, however, do serve to indicate that metals are powerful pro-oxidants; they serve also to give a comparison between the activities of various metals commonly used in plant construction, and the advantage to be had by using tin or tinned metal wherever possible.

Effect of liver preservatives on stability of oils

As far as could be ascertained, very little has ever been done on the storage stability of oils produced from fish or fish livers which had been preserved in different ways.

Drummond and Hilditch[7] indicate the relationship between time of storage of cod livers, and quality of the resulting oil. With increased time of storage of liver, the oils darken, and free fatty acid content rises sharply. This change is probably directly due to the action of natural enzymes in the tissues. Bacterial contamination can likewise cause degradation due to the action of enzymes secreted by bacteria. The production of lipases and lipoxidases by micro-organisms has been shown[8] to cause fat-splitting and oxidative rancidity.

TABLE II

Decrease in $E^{1\ per\ cent}_{1\ cm.}$ 328 mμ and induction period (I.P.) of liver oil stored in contact with various metals.

No.	Metal	Induction period				$E^{1\ per\ cent}_{1\ cm.}$ 328 mμ				Per cent drop in $E^{1\ per\ cent}_{1\ cm.}$ 328 mμ
		1 0	2 3 *months*	3 6 *months*	4 9 *months*	0	3 *months*	6 *months*	9 *months*	
1	Control	3·2	3·1	2	2	5·35	5·12	5·25	5·20	2·8
2	Copper	0·6	0·2	0·2	0·2	5·35	2·82	1·09	0·65	87·7
3	Lead	1·3	0·6	0·2	0·2	,,	4·88	3·83	3·31	38·1
4	Galvanized iron	1·8	0·7	0·2	,,	,,	4·70	4·71	4·33	19
5	Aluminium	2	0·7	0·3	,,	,,	4·70	4·07	3·71	30·6
6	Mild steel	2·2	0·7	0·3	,,	,,	4·81	4·13	3·85	28
7	Chrome steel	1·8	0·5	0·3	,,	,,	4·70	3·64	3·32	37·9
8	Chrome nickel steel	1·7	0·5	0·3	,,	,,	5·06	4·23	4·13	22·8
9	Tin	2	0·6	0·4	,,	,,	4·60	4·57	4·48	16·2
10	(Rubber)	2·6								
11	Rusted steel	1·1								
12	Brass	0·7								
13	Copper plus 0·1 per cent citric acid in oil	1·4								
14	5 p.p.m. copper (as CuCl) plus 0·1 per cent potassium citrate plus 0·1 per cent citric acid	0·4								
15	Copper plus 0·1 per cent cupron ...	1·1								
16	5 p.p.m. copper (as CuCl) plus 0·1 per cent cupron	0·3								
17	Control plus 0·1 per cent cupron ...	3·1								
18	Control plus 1 per cent old oxidised oil	1·7								

Note: In samples 2–13 and in No. 15, strips of metal were used, as described. In Nos. 14 and 16, cuprous chloride was added to the oil. Citric acid and potassium citrate were added as alcoholic solutions. Induction periods in column 1 only determined in contact with metals. All further samples stored in contact with metals, but I.P. determined on oil out of contact with metal.

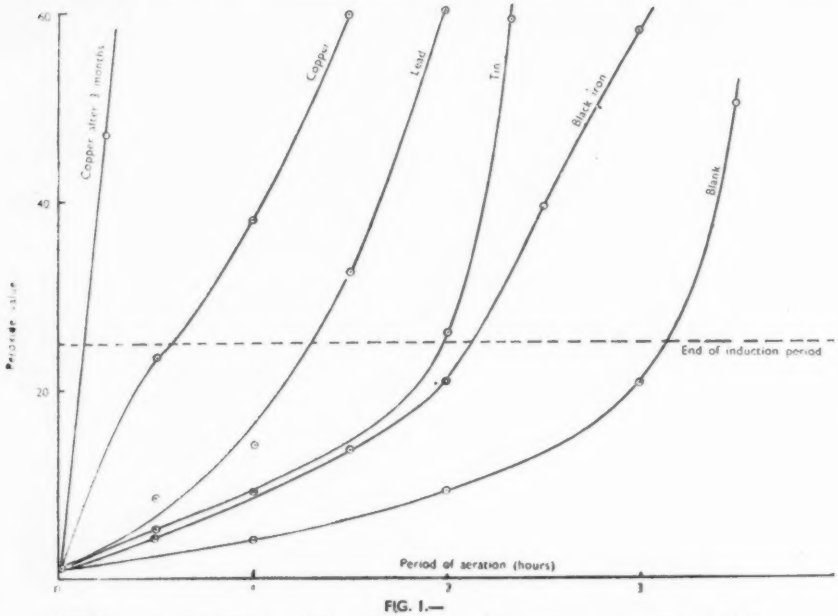

FIG. 1.—
Development of Poroxides during aeration in the presence of metals (100°C.)

Modern methods of liver oil production involve the use of alkalis and temperatures of 100°C., and it can be assumed that free fatty acids will be neutralized, and all micro-organisms inactivated under these conditions. However, we can never be sure that the resulting oil will be free from traces of degradation products formed by oil-attacking organisms acting on the protein material of the liver, and that these impurities may not be just enough to catalyse further oxidative deterioration, as reported by Lea[9] in the case of pork fat.

The products of metabolism or putrefactive bacteria include such odorous materials as amines, skatole and indole[8], fatty alcohols, etc., which are oil-soluble and will undoubtedly affect the quality of the oil, and may catalyse further decomposition.

A storage test has been carried out with samples of oil obtained from liver samples preserved in different ways[10]. All samples were stored in stoppered, completely-filled glass containers, in a dark cupboard, in order to rule out the catalytic effects of light and atmospheric oxygen. The samples of oil were not de-aerated or treated in any other way. At intervals of three months the induction period and vitamin potency of each sample were determined. The results are summarized in Table III.

The samples of liver were pickled in preserving solution, unless otherwise stated.

Discussion on results in Table III

(i) The variation in $E_{1\text{ cm.}}^{1\text{ per cent}}$ 328 mμ values of the samples is significant. The potency of any sample undoubtedly depends on degree of preservation. Fur purposes

TABLE III

Decrease in induction period (I.P.) and potency ($E^{1\ per\ cent}_{1\ cm.}$ 328 mμ) during storage of oils from livers preserved in different ways.

No.	Preservative used with liver (Period of storage, 7 days) (Per cent calculated on weight of liver)	Induction period of oil					$E^{1\ per\ cent}_{1\ cm.}$ 328 mμ					Total drop in I.P. (per cent)	Total drop in potency (per cent)
		0	3 months	6 months	9 months	12 months	0	3 months	6 months	9 months	12 months		
1	Control, *i.e.*, processed immediately	2·8	2·6	2·5	2·2	2	28·5	27·3	26	26·7	26·5	29	7
2	No preservative—storage at room temperature	1	0·4	0	—	—	29·6	29·3	27·6	26·9	26·0	100	12·2
3	No preservative but stored at 0°C.	2·1	2	1·9	1·8	1·7	28·1	27·5	27·6	27·1	26·5	19	5·7
4	1.0 per cent dry borax	2·3	2	1·8	1·8	1·7	29·6	28·1	27·6	27·6	27·1	26	8·5
5	1.0 per cent borax in sea water ...	2·5	2·1	2	1·9	1·7	29·8	28·5	27·7	27·5	27·2	32	8·7
6	0·1 per cent borax in sea water	2·2	2·2	1·5	0·5	—	28·6	28	26	25·7	25·0	100	12·6
7	0·25 per cent formalin (40 per cent) in sea water	2·6	2·1	2·2	2	2	27·9	27·2	26·8	26·2	26·2	23	6·1
8	0·25 per cent formalin in 10 per cent salt water	2·7	2·2	2·2	2·3	2	29·2	27·9	27·9	28·2	28·1	26	3·8
9	0·1 per cent sodium nitrite in sea water	2·5	2·1	1·9	2	1·8	28	28·6	27·3	27·1	26·6	28	5
10	0·1 per cent sodium nitrite in 10 per cent salt water	2·7	1·9	1·8	1·9	1·7	29·7	28·8	27·2	27·4	27·1	37	8·8
11	0·1 per cent sodium nitrite plus 0·1 per cent hydroquinone in sea water	2·3	2	1·9	1·9	1·7	29·9	29·1	28·8	28·3	28·0	26	6·4
12	0·5 per cent sodium sulphite in sea water	1·4	1·4	0·5	0	—	28	27·7	26·1	25·8	25·3	100	9·6
13	0·5 per cent sodium sulphite in 10 per cent salt water ...	2·1	2	1·6	1·7	1·5	28·8	28·4	28·5	28·2	27·9	29	3·1
14	0·5 per cent sodium sulphite plus plus 0·1 per cent butyl gallate in sea water	1·4	1·2	0·5	0	—	27·7	26·7	26	26·1	25·8	100	6·9

of this test, however, loss of vitamin A during storage is more important than loss during preservation of liver.

Note the smaller losses, during storage, in oils from some of the well-preserved samples of liver (Nos. 7, 8, 9) and on the other hand the bigger loss in oil from unpreserved liver (No. 2).

On the whole, more significant results are obtained from a consideration of drop in induction periods, and these are more important, as induction period gives a direct measure of susceptibility to oxidation.

(ii) From a consideration of initial induction periods, it appears that the efficiency of any preservative can be judged by the induction period of the recovered oil, and that the absence of preservative is clearly demonstrated by the low stability of unpreserved material, *viz.*, No. 2, which was further reduced to practically nothing after three months. The loss of potency over a period of one year is also considerable in this sample. The control, *i.e.*, freshly-processed liver, has the highest induction period, and remained very stable during storage. Against this, the sample of liver stored at 0°C. for a week, yielded an oil with lower stability, judged by induction period, but did not lose more vitamin A during storage—in fact, slightly less than the freshly-processed oil.

The well-preserved samples, *i.e.*, those preserved with borax, formalin and nitrite, had induction periods of 2·2 – 2·7 hours, and these never dropped below 1·7 hours during storage. Lower stabilities were obtained from the samples preserved with sulphite, and only sulphite in 10 per cent salt water produced an oil of I.P.=2. Note, too, that the poorly-preserved samples quickly lost all resistance to oxidation.

(iii) After one year only the oils from liver preserved with formalin have two-hour induction periods.

(iv) The oil from liver with 0·1 per cent. borax appeared to be quite stable. After three months, however, there was a sharp decrease in induction period and the total loss of vitamin amounted to over 12 per cent, which is high under these favourable storage conditions.

(v) The most obvious inference to be drawn from these results is that proper preservation of fish livers is an important matter, and requires careful control. Quite apart from the point of quality or physical appearance of the oil, proper preservation of liver has a marked bearing on storage stability of the oil and vitamin A content.

In Fig. 2, a graphical illustration is given of peroxide development (during aeration at 100°C.) of oils from preserved and unpreserved samples of liver. The prolongation of induction period caused by preserving liver with formalin is significant, the rate of peroxide development being the same as in freshly-extracted oil. Storage at low temperatures (0°C.) is less effective, and the much more rapid development of peroxides in oil from unpreserved liver is striking.

The effect of production methods and refining on stability of liver oils during storage

Vegetable oils, which are as a rule much more stable than fish oils, can be refined to produce a palatable product without great concern about the effect of such treatment on the susceptibility of the oil to oxidation.

In fish liver oils, however, where the slightest decrease in induction period means increased danger of destruction of vitamin A, a careful investigation has to be made of the influence of refining methods on stability.

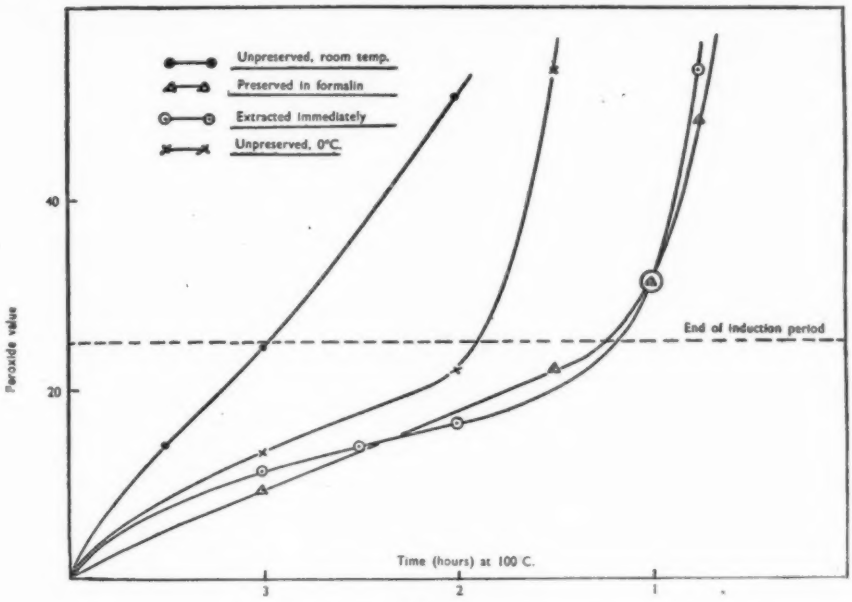

FIG. 2.—
Peroxide development in oils from preserved and unpreserved samples of liver.

Mattill and Crawford[11] have shown that acid and alkali treatments, and decolorizing processes, can shorten the induction period of crude maize oil considerably. With pilchard oil[12] the same effects were noticed, and a preliminary storage test indicated that such refined oils, after one month's storage, readily absorbed oxygen. Holm *et al.*[13] advanced the theory that such a reduction of induction period is due to destruction or removal of natural anti-oxidants. This explanation is now generally accepted, and is indeed easily understood in the case of alkali refining, which is bound to destroy phenolic inhibitors, the best-known class of antioxidants[14].

Brocklesby[15] points out that alkali or acid treatment increases the rate of peroxide formation in oils of low unsaturation, and completely removes the induction period in more highly unsaturated oils.

The effect of refining is seen at low temperatures as well as in accelerated degradation tests, and it has been reported that there is much more rapid peroxide development in refined soybean oil during storage at 80°F. than in crude oil.

It was decided then to compare the stabilities of primary and refined shark liver oils, and to determine any further decreases in induction period and vitamin potency in these oils during storage for one year.

For this experiment a sample of fresh primary liver oil was selected and refined in several ways[16], *i.e.*, alkali refined, bleached with terra silicea (diatomite), decolorized with Merck's clarocarbon, and steam-vacuum deodorized. Induction periods and vitamin A potencies of all samples were determined, and the results were compared with those obtained from a few commercial samples of primary and refined vegetable

oils. The vegetable oils had been subjected to alkali treatment, and steam-vacuum deodorization, and were not treated in any other way for the purpose of these tests. The results are given in Table IV. Induction period was determined by aeration at 100°C. and a peroxide value of 25 accepted as the end of the induction period.

TABLE IV

Induction periods of crude and refined fish liver and vegetable oils.

Raw material	*Method of refining*	*Induction period (hours)*	*Decrease in I.P. during processing (per cent)*
Shark liver oil	— (primary)	2·4	—
do.	Steam-alkali	1·2	50·0
do.	Decolorized—carbon ...	1·4	41·5
do.	Bleached—diatomite ...	1·5	37·5
do.	Steam—vacuum	1·4	41·5
Arachis oil I—30/8/45	— (crude)	2·7	—
do.	Alkali plus steam—vacuum	2·2	18·5
Arachis oil II—29/11/45	— (crude)	3·1	—
do.	Alkali plus steam—vacuum	2·1	32·2
Arachis oil III—20/11/45	— (crude)	6·0	—
do.	Alkali plus steam—vacuum	5·0	16·7

Observations

(i) A considerable variation in induction periods of commercial arachis oils, even over a short period of three months (all samples from a reputable producer), but

(ii) a consistent shortening of induction period caused by refining these samples.

(iii) A considerable shortening of induction period in all the refined shark liver oil samples, indicating the adverse effect of all refining processes. It appears that the natural induction period is reduced by about 35 – 50 per cent.

The results in Table V illustrate the decrease in potency and induction period during storage of these refined oils.

The unrefined blank lost about 50 per cent. of its natural resistance to oxidation, and the vitamin potency decreased by 12 per cent during storage for 12 months.

The alkali refined sample lost only 16 per cent of its vitamin A, which is relatively low if one remembers that refining caused no destruction of the vitamin. During storage for one year the induction period decreased by only 25 per cent, but then alkali refining caused a 50 per cent decrease at the start, and the final sample, with an induction period of less than one hour, can be regarded as very unstable and susceptible to oxidation.

The carbon-decolorized oil lost practically all resistance to oxidation after six months' storage, while its vitamin potency decreased by 18 per cent, and this, in addition to a processing loss of 6 per cent, indicates that carbon decolorization is perhaps the most harmful refining process to which a liver oil can be subjected.

There is little difference between the bleached and steam-vacuum deodorized samples. In both experiments, a loss of 2 per cent of the vitamin A occurred during refining, a further 15 – 17 per cent during storage, while the induction period was shortened by about 40 per cent during processing and a further 40 per cent during storage.

These experiments serve to verify the adverse effects of refining methods, and to indicate the danger of losing vitamin A during production or storage of refined liver oils, unless suitable precautions are taken.

As far as the use of alkalis in the production of liver oils is concerned, the destruction of natural inhibitors is not so marked. It has been shown[16] that liver oils with induction periods of 3 - 3·5 hours can be produced by the alkali-digestion method. This can probably be explained by considering that the alkali is present in much more dilute solution during alkali-digestion of livers than during alkali-refining of the oil, with consequent less danger of destroying natural inhibitors.

Effect of dissolved air on stability during storage and protection obtained by using inert gases

The use and practicability of inert atmospheres have often been described, but reports have been rather conflicting. Emery *et al.*[17] found that an atmosphere of carbon dioxide does not prevent the development of rancidity in fats. Neither nitrogen nor carbon dioxide were found[7] to retard oxidation in cod liver oil, but the latter experiment was carried out by merely filling the head space above the oil with the gas under examination.

On the other hand, Callow[18] has found marked protection of bacon fat by storage in carbon dioxide. Fats stored in the gas did not develop rancidity during storage for twelve months, while control samples, stored under atmospheric conditions, were quite rancid after four months.

An attempt has been made to compare the storage stability of an oil saturated with air, *i.e.* as produced commercially, with the stabilities of oils in which all air had been replaced by nitrogen and carbon dioxide.

A fresh commercial shark liver oil was selected and portion of it stored in completely-filled glass bottles. No head space was left, as the object was to determine the effect of dissolved air only.

A further portion of this oil was repeatedly evacuated at 100°C., and then cooled to room temperature in an atmosphere of carbon dioxide, to saturate it with the gas at ordinary temperature. The oil was stored in completely-filled bottles, which were inverted to provide an oil seal at the stopper. In the same manner a further portion of the oil was saturated with nitrogen, and all samples were stored in a dark cupboard at room temperature.

At regular intervals (three months) a sample bottle of each oil was removed and induction period and vitamin potency determined. The results are summarized in Table VI.

Discussion

Although this test has only been carried out on a single specimen of oil, the results are significant. There is very good agreement between the results obtained with carbon dioxide and nitrogen, both samples of oil being much better than the sample containing dissolved air.

TABLE V

Decrease of potency ($E^{1\ per\ cent}_{1\ cm.}$ 328 mμ) and induction period (I.P.) in crude and refined samples of shark liver oil during storage at room temperature.

Samples	*Induction period*					$E^{1\ per\ cent}_{1\ cm.}$ 328 mμ					*Total drop in I.P. (per cent)*	*Total drop in* $E^{1\ per\ cent}_{1\ cm.}$ *328 mμ (per cent)*
	0	3 *mths.*	6 *mths.*	9 *mths.*	12 *mths.*	0	3 *mths.*	6 *mths.*	9 *mths.*	12 *mths.*		
Original oil (primary)	2·4	1·9	1·5	1·3	1·3	9·95	9·64	9·38	8·97	8·73	46	12·3
Alkali, refined	1·2	1·2	1·1	1·1	0·9	9·96	9·84	9·47	8·74	8·35	25	16·2
Decolorized (Merck's clarocarbon) ...	1·4	1·2	1·0	0·4	0·0	9·32	9·12	7·98	7·98	7·63	100	18·1
Bleached (diatomite)	1·5	1·2	0·6	1·0	0·9	9·75	9·57	9·15	8·47	8·25	40	15·4
Steam—vacuum deodorized	1·4	1·1	1·2	1·0	0·9	9·71	9·61	9·33	8·68	8·08	36	16·8

TABLE VI

Variations in induction period (I.P.) and vitamin potency ($E^{1\ per\ cent}_{1\ cm.}$ 328 mμ) of liver oil stored in air, nitrogen and carbon dioxide.

Period of storage	*CONDITIONS OF STORAGE*					
	Air		*Nitrogen*		*Carbon dioxide*	
	I.P.	$E^{1\ per\ cent}_{1\ cm.}$ 328 mμ	*I.P.*	$E^{1\ per\ cent}_{1\ cm.}$ 328 mμ	*I.P.*	$E^{1\ per\ cent}_{1\ cm.}$ 328 mμ
0 ...	2·4	9·95	2·4	9·95	2·4	9·95
3 months	1·9	9·64	2·1	9·91	2·1	9·90
6 months	1·5	9·38	2·1	9·80	2·1	9·82
9 months	1·3	8·97	2·1	9·04	2·1	9·16
12 months	1·3	8·73	1·9	9·00	2·0	9·10
Total decrease (per cent)	46	12·3	21	9·6	17	8·5

The decrease in induction periods of samples stored in inert atmospheres is only 17 – 20 per cent, as against 46 per cent for the control, and the loss of vitamin A is also much smaller. It must be borne in mind that the raw material was a plant sample of liver oil which may not have been produced from good fresh liver. This oil had also been in contact with iron digestors and storage tanks, and the degree to which further deterioration is retarded in such an oil clearly indicates the beneficial effect of storage in inert atmospheres.

In plant operation this could be done by de-aeration of freshly-produced oil by simple means and breaking the vacuum with carbon dioxide or nitrogen. In addition the head-space in drums or storage tanks can be filled with the gas.

It was observed that samples stored in nitrogen and carbon dioxide exhibited delayed stearin separation during the whole period of storage. In the control, stearin was quickly deposited, and settled within two weeks, to a thin, firmly-packed layer at the bottom of all containers. After a year the samples stored in inert atmospheres were sparkling and clear and there was no sign of "stearin".

Effect of light on oxidative rancidity

No work has been done on the effect of light in promoting deterioration of fish oils as the commercial production of liver oils is usually organized in such a manner that the oil is very seldom exposed to direct light.

However, a very brief review of the literature on this subject will be given in order to complete the review of factors influencing the stability of fish liver oils.

Ziels and Schmidt[9] show that strong light, mainly the portion of the spectrum between 325 and 460 millimicrons, causes a marked deterioration in flavour and odour.

Coe[19] suggests that rancidity is due to photochemical activity of light. The pigments of animal or vegetable fats are photosensitive and may cause the formation of an unstable hydrogen peroxide which decomposes to form peroxides in the fat. The initiation of such a chain reaction can occur during the very short periods when an oil is exposed to light.

Lowen *et al.*[20] found that when oils were kept in stoppered bottles and exposed to diffuse daylight no relation between peroxide formation and vitamin A destruction

could be obtained, indicating that a different mode of autoxidation is catalysed in the presence of light.

The action of direct sunlight, diffused daylight, and electric light on acceleration of oxidation in beef-kidney fat is strikingly illustrated by Lea[21].

From the foregoing it is apparent that light can act as an oxidation accelerator, and that fish liver oils, or the livers, should not be exposed to light unnecessarily, and never to direct sunlight.

Effect of moisture on storage stability of shark liver oils

Although much work has been done on the influence of moisture on the deterioration of products containing fats, oils, and non-fat constituents there are surprisingly few data available on the influence of moisture on stability of pure fats.

While it has been found[22] that water increased the induction period of butter-fat at 95°C., no influence could be detected on the induction period of lard[23]. Lea[24] found that water shortened the induction period of lard stored in glass.

In a single experiment, King *et al.*[25] found that the part taken by moisture in the development of oxidative rancidity as compared with other influences was negligible.

It was decided to carry out a storage test in order to investigate the effect of moisture on stability.

Commercial liver oils normally contain 0·1 – 0·25 per cent moisture and it would serve no useful purpose, from a practical point of view, to study the effect of higher moisture content than this. The lower limit of moisture is determined by the moisture content of vacuum-dried oils and this is usually 0·01 – 0·001 per cent. So for the purpose of this test two commercial oils A and B were selected and their moisture content determined. These oils were then vacuum-dried at 100°C. for one hour, after which the moisture content was again determined using the modified Smith-Bryant method[26].

The induction periods and vitamin A potencies of these oils were determined which were then stored in completely-filled sealed bottles, so that the moisture content could not change during storage. At three-monthly intervals these determinations were carried out. The results are recorded in Table VII.

Moisture contents were as follows:—

Oil A dry	0·006	per cent.
Oil A moist	0·21	do.
Oil B dry	0·01	do.
Oil B moist	0·23	do.

Discussion

From the results in Table VII it is apparent that the total decrease in induction period is less in a "dry" oil than in a normal "moist" liver oil. In sample A the difference is very significant, but even in sample B, the vacuum-dried oil was more stable than the "moist" oil after nine months.

As far as vitamin potency is concerned, the total loss in oil A is slightly higher in the dried sample, but in oil B, the dried sample suffered a slightly smaller loss of vitamin A during storage.

On the whole these results suggest a mechanism of degradation whereby moisture increases the susceptibility to oxidation without causing a corresponding influence on the vitamin A content directly.

TABLE VII

Variations in induction period (I.P.) and vitamin potency ($E_{1\,cm.}^{1\%}$ 328 mμ) during storage of dry and moist shark liver oil.

Period of storage	*Description of sample*			
	Oil A dry	*Oil A moist*	*Oil B dry*	*Oil B moist*
(*a*) *Induction period*:				
0	3·9	3·9	3·2	3·2
3 months	3·7	3·7	3·1	3·0
6 months	3·5	2·9	3·1	2·9
9 months	3·5	2·8	2·6	2·4
Total drop (*per cent*)	10·3	28·1	18·7	25·0
(*b*) *Vitamin A potency* ($E_{1\,cm.}^{1\%}$ 328 mμ)				
0	22·50	22·50	23·51	23·51
3 months	21·70	21·61	23·45	23·16
6 months	20·43	20·72	22·90	22·88
9 months	20·01	20·20	21·72	21·33
Total drop (*per cent*)	11·1	10·2	7·7	9·3

Summary—Precautions to be taken in the production and storage of fish liver oils

For the benefit of those concerned with the production of fish liver oils a summary will be given of the precautions to be taken in this industry. The commercial producer of fish oils can never exercise too much care in controlling the conditions of production and storage and only by taking all possible precautions, at every stage, can a good and stable oil be produced and loss reduced to a minimum.

The following precautions are necessary:

(1) The gall bladder should be opened and the bile extruded immediately the liver is taken out of the fish. The liver should then be rinsed in clean sea water and immediately placed and weighted down in a preservative solution of sea water containing 0·25 per cent formalin (40 per cent) on the weight of liver, and 1 part in 2,000 sodium nitrite. If the livers are being collected in a 45-gallon drum the drum should contain about 4 – 6 gallons of water in which is dissolved 1 – 2 lbs. commercial formalin, and ½ – 1 oz. sodium nitrite. The lid of this drum should never be left off and full drums of liver should always be stored below deck out of the heat and light of the sun.

Alternatively, the washed liver can be rolled in powdered borax but this must be done carefully, not haphazardly, to ensure thorough contact.

(2) While bearing in mind the practical difficulties, the necessity of landing and processing the livers with as little delay as possible, is stressed.

(3) Absolute cleanliness of equipment is essential.

All run-ways and machinery should be hosed and "steamed down" while digestion and storage tanks as well as containers for the liver, should be

spotlessly clean and sprayed with a dilute solution of formalin. "Stickwater" contains dissolved protein which is an excellent medium for growth of bacteria and should not be allowed to dry on the surfaces of containers. Care should be taken that a "ring" of oil never forms in settling or digestion tanks, as this will oxidize quickly and contaminate later batches.

(4) The use of tin or heavily tinned metal is recommended for construction of all containers, including drums for collection of livers. On no account should copper or brass be used and corroded iron surfaces must be avoided.

(5) If the livers were particularly old and the separated oil is dark and rancid alkali-refining will improve the quality considerably.

(6) The incorporation of suitable antioxidants should be regarded as an essential step in production. There are so many factors which affect the stability of liver oils adversely that artificial means of counteracting this is essential.

(7) If oils are to be stored for periods exceeding three months, de-aeration and saturation with nitrogen or carbon dioxide will be beneficial.

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